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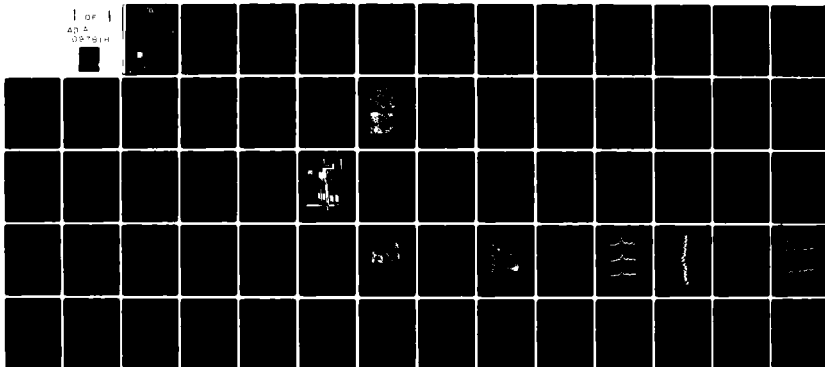
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**MATERIALS RESEARCH FOR ADVANCED  
INERTIAL INSTRUMENTATION**

**TASK 3: RARE EARTH MAGNETIC MATERIAL  
TECHNOLOGY AS RELATED TO  
GYRO TORQUERS AND MOTORS**

**DECEMBER 1980**

**TECHNICAL REPORT NO. 3  
FOR THE PERIOD  
1 OCTOBER 1979 - 30 SEPTEMBER 1980**

**BY**

**D. DAS, K. KUMAR, AND E. WETTSTEIN**

**Prepared for the Office of Naval Research, Department of the Navy,  
Under Contract N00014-77-C-0388**

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| 20. ABSTRACT (Continue on reverse side if necessary and identify by block number)<br>Hot isostatic pressing (HIP) of SmCo <sub>5</sub> magnets can now be considered a viable alternative to sinter technology. Qualities of magnets are usually better. Even in as-HIPed condition the magnetic properties compare favorably with commercial sintered magnets. Thermal optimization following the HIP procedure further improves the properties. Unique in these magnets, as opposed to sintered magnets, are the consistently high H <sub>k</sub> values obtained over the<br>(Continued on reverse side) |  |  |

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entire composition range of 35.5 to 37.0 weight percent Sm. It was interesting to note that the higher Sm compositions showed very little degradation of coercivity on slow cooling from aging temperature.

Flux decay rates were measured on a sinter magnet (which showed high  $H_{ci}$  and  $H_k$ ) and a HIPed magnet (which was prepared from large particle size powder). Different thermal treatments were given to the magnet samples prior to magnetization and testing. The best results obtained corresponded to decay rates of 280 ppm/decade of days for the sinter magnets and 161 ppm/decade of days for the HIPed magnets. These low rates of decay were obtained when the samples were slow cooled following the aging treatment at 900° C.

Initial sinter experiments were performed to determine the compositions necessary to obtain zero temperature coefficient using  $ErCo_5$  and  $TbCo_5$  to replace part of  $SmCo_5$ . The zero compositions were determined; however the energy products corresponding to these compositions were low. Attempts are now being made to obtain higher values for the energy products by using the HIP technique.

Our highest energy product magnets prepared by HIP (21 MGOe) and sinter technique (18 MGOe) were measured for thermal expansion coefficient and found to have values within two percent of that of beryllium. There is, therefore, no need to sacrifice a part of the energy product to match the thermal expansion coefficients.

Investigation of the fabrication feasibility of  $Sm_2Co_{17}$ -type binary composition magnets with coercivities well in excess of those achievable by sintering procedures was included in this program in October 1979. Initial experiments showed that deposits which exhibit x-ray diffraction patterns characteristic of amorphous materials can be produced using this process in the composition range of interest. The possibility of producing magnets with the easy magnetization axis of the  $Sm_2Co_{17}$  phase oriented perpendicular to the plane of the deposit was indicated in some of the x-ray data. It was tentatively concluded that the cooling conditions at the substrate substantially affected the texture in the deposit. Low temperature treatments, which employed temperature as well as time at temperature variations, of the several deposited materials showed that coercivities substantially higher than the 1 to 2 kOe typically observed for the sintered " $Sm_2Co_{17}$ -type" materials could be produced by this technique. The largest  $H_{ci}$  value measured in this program was for a deposit containing about 29.0 weight percent Sm (after making corrections for the estimated loss to evaporation and oxidation). This value was 7.9 kOe and was measured after exposing the deposited material to 600°C for 48 hours. The other magnetic properties of this deposit were  $B_R = 6500$  G,  $H_C = 4050$  Oe, and  $(BH)_{max} = 6.6$  MGOe. Controlled crystallization studies on the amorphous deposits and deposition at temperatures other than those employed so far are planned.

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## SECTION 1

### INTRODUCTION

#### 1.1 Program Background

The Charles Stark Draper Laboratory, Inc. (CSDL) is involved in research and development over a broad spectrum of technology associated with guidance, navigation, and control for vehicles of all types. One of the areas of importance to advancements in inertial navigation systems is the improvement of magnetic devices serving critical functions in these systems. Samarium-cobalt magnet devices are used within inertial systems as components of the inertial instruments or sensors - the gyro and accelerometer - and as gimbal torque motors. As an example of the former category, samarium-cobalt permanent magnets are employed in the torque generator, or angular motion forcer, of the movable and buoyant member of the instrument. The torque generator is of cylindrical geometry, and in many designs the magnets are located on the moving member which must remain buoyant in fluid. Here the lower volume of the magnet impacts favorably on the overall size and weight of the completed instrument.

Rare-earth cobalt magnets, because of their large maximum energy product,  $(BH)_{\max}$ , are ideally suited for many other applications requiring high magnetic strength. Because of the large  $(BH)_{\max}$  a lesser volume of magnet is required to produce a given amount of magnetic flux in a device.

In addition to their high energy product, magnets utilized in precision inertial instruments must also possess excellent long-term flux stability, insensitivity to temperature change, and physical properties compatible with beryllium. Because of its favorable strength-to-weight ratio, beryllium is the structural material of choice in modern inertial instruments.

A comprehensive program to develop samarium-cobalt magnets by powder-metallurgy techniques for applications as components in new and future generations of inertial instruments was initiated at the Draper Laboratory in October 1977 under the sponsorship of the Office of Naval Research. The objectives of the program were to develop improved sintering procedures to fabricate inertial-grade  $\text{SmCo}_5$  magnets with improvements in three areas mentioned above: long-term flux stability, reduced temperature coefficient, and tailoring of the thermal expansion coefficient to match that of beryllium.

During the first two years (October 1977 to September 1979) the efforts in the magnetic materials task of the ONR materials research program focused on sintered and hot isostatically pressed magnets of the  $\text{SmCo}_5$  composition. A new subtask was added as of October 1979 which would concentrate on  $\text{Sm}_2\text{Co}_{17}$  magnets fabricated by the arc-plasma-spray process. The motivation behind this subtask was the earlier achievement of outstanding successes with  $\text{SmCo}_5$  magnets using this process at CSDL.

## 1.2 Objectives

The objectives of the present program are to investigate the arc-plasma spray process for fabricating  $\text{Sm}_2\text{Co}_{17}$ -type magnets and to develop improved sintering procedures to produce inertial-grade  $\text{SmCo}_5$  magnets with improvements in the following areas:

(1) Long-term flux stability at constant temperature (140°F)

Desired: 0.008 ppm/90-day

Present capability: Sintered: ~ 1 ppm/day

Plasma Sprayed: 0.05 ppm/day

(2) Thermal stability of residual induction

Desired: 0.1 ppm/°F

Present capability: 300 ppm/°F

(3) Tailoring of thermal expansion coefficient

Desired, same as beryllium: 6.6  $\mu\text{in./in. } ^\circ\text{F}$

Isotropic: 4.7  $\mu\text{in./in. } ^\circ\text{F}$

(a) Along magnetization direction: 3.1  $\mu\text{in./in. } ^\circ\text{F}$

(b) Normal to magnetization direction: 7.1  $\mu\text{in./in. } ^\circ\text{F}$

## SECTION 2

### PROGRESS PRIOR TO THIS REPORT

Two interim annual reports<sup>(1,2)\*</sup> have been submitted, which described the progress in this area for a period of two years from October 1977 to September 1979. The highlights of this past performance are summarized below.

The three objectives of the program were to incorporate into  $\text{SmCo}_5$  magnets produced by powder metallurgy: (1) high flux stability, (2) near-zero temperature coefficient in the vicinity of the gyro-operating temperature, and (3) tailored thermal expansion coefficient to match that of beryllium. Of the three objectives, the achievement of high flux stability appeared to be the most challenging since there is a lack of adequate scientific understanding of the rather low values of flux stability typically measured in these magnets. Scientific basis for the other two objectives, in contrast, was quite clear<sup>(3,4)</sup> and thus these objectives were considered more easily obtainable than the first one. Efforts during the first two years were therefore concentrated on the first objective, not only to achieve the stated goal but also to develop a scientific understanding of the phenomenon of flux decay in the  $\text{SmCo}_5$  magnets.

Work began on the premise that to achieve high stability the magnets should also possess higher resistance to demagnetization, since the decay of magnetic induction is a demagnetization process. Hence, the values of coercivities, both  $H_{ci}$  and  $H_k$ , required improvement since these are a measure of the magnet's ability to resist demagnetization. Based on the understanding of the mechanisms of demagnetization in  $\text{SmCo}_5$

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\*Superscripted numerals refer to sources in the List of References.

magnets, (5,6) the method of fabrication therefore needed to be improved. This entailed the development of a more sophisticated method of fabrication to maintain fine grain size while lowering the oxygen content in the finished magnet. The two requirements clearly conflicted each other. As a result, a compromise was sought which achieved an optimum combination of grain size and oxygen content.

In line with these requirements, a magnet sintering facility capable of ultra-high vacuum operation ( $10^{-6}$  torr capability at  $1100^{\circ}\text{C}$ ) was designed and built for oxygen-free processing of these magnets. Techniques for producing powder with low oxygen contamination (from the environment) were also developed for this purpose. The total amount of oxygen incorporated into the powder was found to be less than what is obtained with conventional procedures.

This resulted in remarkably high values of  $H_{ci}$  and  $H_k$  in sintered  $\text{SmCo}_5$  magnets produced at Draper Laboratory. The unprecedented value of 29 kOe was measured for  $H_k$  in a few of these magnets as compared to 5 to 10 kOe found in most commercial magnets. The energy-product values of these magnets were, however, limited to about 13 MGOe because of poor alignment. Further investigations were expected to result in substantial improvements in the values of the energy product. By controlling the maximum level of oxygen content to about 0.6 weight percent, along with fine grain size in the final sintered product, we were able to produce some outstanding magnetic properties, such as  $(BH)_{\text{max}} \sim 20$  MGOe,  $H_{ci} \sim 50$  kOe, and  $H_k$  of 33.5 kOe. The result was a low flux decay rate of 700 ppm/decade of days. This translated into a decay rate of less than a ppm/day in the third decade of time, which is the decade of interest. With special stabilizing treatments planned, the stability value was expected to be improved further.

The arc-plasma-sprayed magnets with an oxygen content of about 0.15% possess a low decay rate of 50 ppm/decade. Unfortunately, their energy products are low because of the random grain orientation. Our immediate goal was to produce aligned and densified powder metallurgical

magnets with oxygen content typical of APS magnets. To accomplish that, CSDL developed a hot isostatic pressing process in this program, which resulted in nearly 100% dense magnets of fine and aligned grain structure with little if any oxygen pickup above that of the starting powder compact. Properties of magnets formed with very coarse powder (using this technique) were found to be quite comparable to what is available with sinter technology. With the use of finer-sized powder, magnets with outstanding properties and high flux stability were expected, provided a low level of oxygen could be maintained in the fine powders.

Experiments to determine the flux decay rate were started on some of the high coercivity sintered magnets. These studies were to be expanded to include samples of various magnetic characteristics with the hope of understanding the underlying mechanism of high flux stability. In the ensuing period, efforts were expected to be directed towards temperature compensation and tailoring of thermal expansion along with further studies on stability.

### SECTION 3

#### SmCo<sub>5</sub> MAGNET INVESTIGATIONS DURING THIS REPORTING PERIOD

##### 3.1 Further Studies of Hot Isostatic Pressing (HIP) of SmCo<sub>5</sub>

Important metallurgical considerations for producing high coercivity are believed to be fine grain size and low oxygen content in the sintered body.<sup>(7)</sup> Because of the high temperature (approximately 1120°C) at which the sintering is carried out to achieve the desired degree of densification, there is considerable grain growth in the sintered body. The particle size of powder used is usually between 5 and 10  $\mu\text{m}$ , compared to 20 to 30  $\mu\text{m}$  grain size in the sintered magnet. Finer powder cannot be used without further increasing the oxygen content of 0.5 to 1.0 weight percent found even in these rather coarse powders.

If the densification of the powder could be achieved at temperatures in the range of 900° to 950°C there would be no significant grain growth.<sup>(8)</sup> This can be accomplished only if a compressive force is applied to the powder compact while it is at the densification temperature. Using sinter-grade powder, dense magnets could be produced (ending up with grain size ranging between 5 to 10  $\mu\text{m}$ ) with oxygen content similar to that of sintered magnets made from the same powder. Alternatively, use could be made of powder size as large as is found for the grains in the sintered magnets resulting in similar grain size as standard sintered magnets but with a much smaller oxygen content. In either case an improvement in the magnetic properties is expected.



For these experiments the selected average powder particle sizes were 40 and 25  $\mu\text{m}$ , both produced by the conventional techniques of crushing, pulverizing, and attritor grinding. The 40  $\mu\text{m}$  size powder particle was produced by a short period of final grinding, using the -400 mesh fraction of the powder which was roughly 50 percent of the total. The finer powder with an estimated average particle size of 25  $\mu\text{m}$  was obtained using longer time attritor grinding. Nominal chemical compositions of the powders were adjusted to 35.5, 36.5, 37.5, and 38.5 weight percent Sm for the coarse powder and 35.5, 36.0, 36.5, and 37.0 weight percent Sm for the fine powder by blending the powders of 34.5 percent Sm and 42.0 percent Sm alloys. The blended powders were cold isostatically pressed into 0.5-inch diameter cylindrical rods after alignment in a 140 kOe field Bitter solenoid. The 40- $\mu\text{m}$  size compacts were then transferred to thin-walled stainless steel containers which were evacuated, baked out, sealed, and hot isostatically pressed (HIPed) at 900°C in an argon pressure of 15,000 lb/in<sup>2</sup> for 2 hours. The removal by machining of the magnet samples from the stainless steel container resulted in cracking. This was solved by slicing the assembly into usable size and using EDM to produce specimens for measurement. The problem of cracking encountered with the stainless steel cans was subsequently eliminated by using cold rolled low carbon steel containers for the next batch of samples, which were HIPed at 950°C. To avoid contamination of the alloys during HIP procedure, the cold-pressed compacts were wrapped with thin tantalum foil. The HIPed samples were removed from the container by dissolving the container material in warm dilute HNO<sub>3</sub>. The tantalum foil was then easily removed following this acid solution treatment. Magnetic properties were measured for both 40- and 25- $\mu\text{m}$  samples in the as-HIPed condition as well as after various thermal treatments.

### 3.2. Results and Discussion of SmCo<sub>5</sub> HIP Studies

The magnetic properties of the 40- $\mu\text{m}$  -particle size HIPed magnets are shown in Table 1. Similar data for the 25- $\mu\text{m}$  particles are given in Table 2.

Table 1. Magnetic Properties of 40  $\mu\text{m}$ -particle magnets HIPed at 900°C.

| Thermal Treatment                                | Sm Content<br>Properties | 35.5<br>wt % | 36.5<br>wt % | 37.5<br>wt % | 38.5<br>wt % |
|--|--------------------------|--------------|--------------|--------------|--------------|
| As HIP'ed  | $B_r$ (kG)               | 7.9          | 7.9          | 7.1          | 7.2          |
|  | $H_{ci}$ (kOe)           | 4.0          | 5.0          | 5.0          | 5.0          |
|  | $H_k$ (kOe)              | 1.5          | 4.0          | 4.0          | 4.0          |
|  | $(BH)_{\max}$ MGOe       | 6            | 10           | 8            | 9            |
| 75 h at<br>1000°C<br>+ 900°C 4 h<br>Quick Cooled | $B_r$ (kG)               | 8.1          | 7.9          | 7.1          | 7.2          |
|  | $H_{ci}$ (kOe)           | 27.0         | 25.0         | 8            | 5            |
|  | $H_k$ (kOe)              | 12.0         | 7.0          | 5.0          | 8.0          |
|  | $(BH)_{\max}$ MGOe       | 16           | 14           | 11           | 9            |
|  | % Theor.<br>Density      | 99.1         | 99.2         | 99.8         | 100.0        |

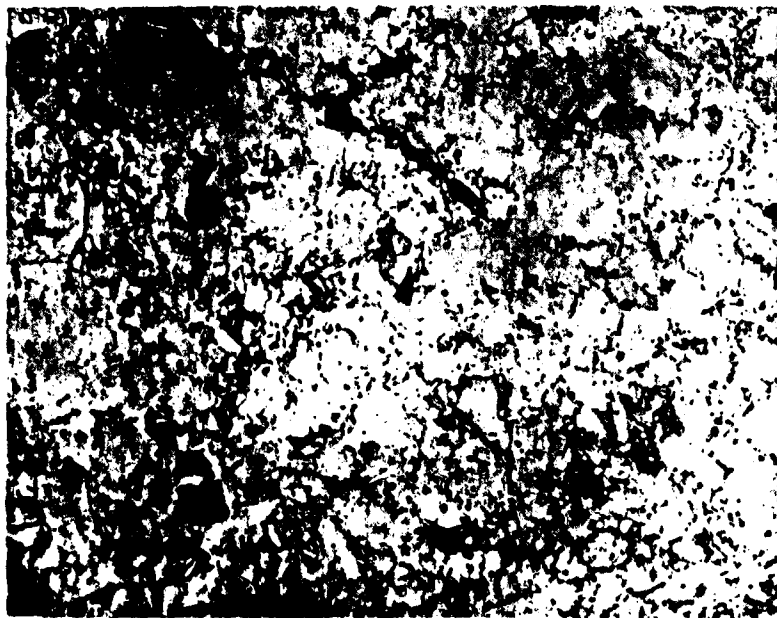
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In the as-HIPed condition the magnetic properties of 40- $\mu\text{m}$  powder are poor and comparable to those of the raw powder. This indicated that the exposure to 900°C for 2 hours in HIP provided little or no healing of the damaged powder particles. However, it did produce a near-theoretical density with no grain growth. Figure 1 is an optical micrograph of the 35.5 percent Sm magnet of Table 1. The light grains are  $\text{SmCo}_5$  and the darker ones are  $\text{Sm}_2\text{Co}_7$ . The thermal treatment shown in Table 1 produced large increases in the coercivities of the 35.5 and 36.5 weight percent Sm magnets without changing the  $B_r$ , the grain size, or the grain morphology. These values are considered significant for magnets prepared out of such large particles of  $\text{SmCo}_5$  powder. The high Sm-content alloys, however, did not show similar improvement in properties. Therefore, it was decided to investigate the range between 35.5 and 37.0 weight percent Sm with a somewhat smaller powder particle size (25  $\mu\text{m}$ ) HIPed at a slightly higher temperature (950°C). Near-theoretical density was reached, once again, with little grain growth.

Table 2. Magnetic Properties of 25  $\mu$ m-particle magnets HIPed at 950°C.

| Thermal Treatment                         | Sm Content<br>Properties | 35.5 | 36.0 | 36.5 | 37.0 |
|---|--------------------------|------|------|------|------|
|   |                          | wt % | wt % | wt % | wt % |
| As- HIPed                                 | $B_r$ (kG)               | 8.9  | 8.6  | 8.6  | 8.4  |
|   | $H_{ci}$ (kOe)           | 20   | 19   | 18   | 20   |
|   | $H_k$ (kOe)              | 10   | 10   | 8    | 7    |
|   | $(BH)_{max}^{MGOe}$      | 20   | 19   | 17   | 16   |
| 950°C-62 h<br>Quick Cooled                | $B_r$ (kG)               | 9.2  | 8.6  | 8.7  | 8.6  |
|   | $H_{ci}$ (kOe)           | 36   | 36   | 34   | 35   |
|   | $H_k$ (kOe)              | 19   | 14   | 12   | 10   |
|   | $(BH)_{max}^{MGOe}$      | 21   | 18   | 18   | 18   |
| As Above<br>Furnace<br>Cooled             | $B_r$ (kG)               | 9.1  | 8.7  | 8.9  | 8.7  |
|   | $H_{ci}$ (kOe)           | 18   | 26   | 29   | 31   |
|   | $H_k$ (kOe)              | 6.5  | 8.0  | 7.5  | 8.5  |
|   | $(BH)_{max}^{MGOe}$      | 18   | 17   | 17   | 17   |
| 1050°C-24 h<br>900°C-24 h<br>Quick Cooled | $B_r$ (kG)               | 9    | 8.5  | 8.7  | 8.6  |
|   | $H_{ci}$ (kOe)           | 33   | 35.5 | 33.5 | 33.5 |
|   | $H_k$ (kOe)              | 26   | 20   | 17.5 | 18   |
|   | $(BH)_{max}^{MGOe}$      | 20   | 20   | 10   | 18   |
| 1108°C-3 h<br>900°C-24 h<br>Quick Cooled  | $B_r$ (kG)               | 8.9  | 8.6  | 8.7  | 8.4  |
|   | $H_{ci}$ (kOe)           | 33.5 | 36   | 33   | 32.5 |
|   | $H_k$ (kOe)              | 25   | 24   | 18   | 17   |
|   | $(BH)_{max}^{MGOe}$      | 20   | 18   | 18   | 17   |
|   | % Theor.<br>Density      | 98.7 | 99.1 | 98.7 | 99.3 |

2/81 CD22607

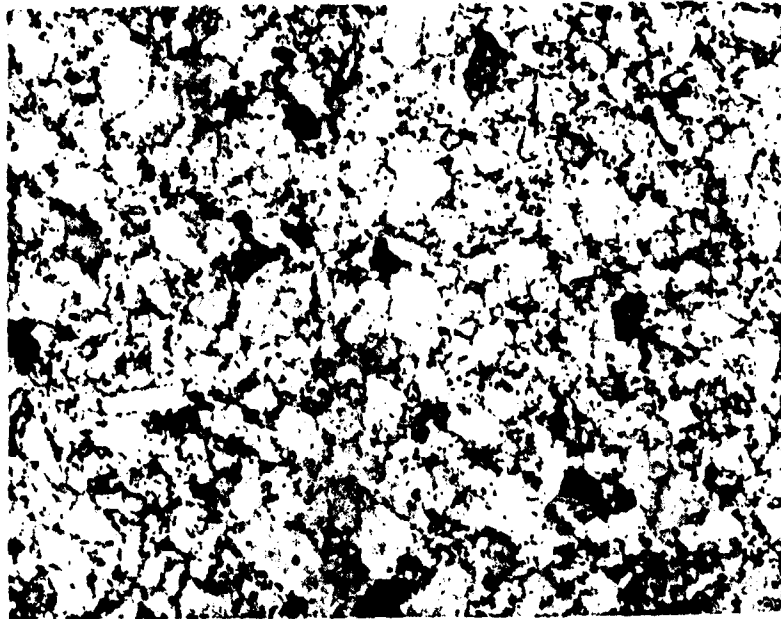


OPTICAL MICROGRAPH OF 40  $\mu\text{m}$  PARTICLE  
SIZE HIP'ed MAGNET AFTER TREATMENT  
AT 1000 °C FOR 75 HOURS. NOMINAL COMPO-  
SITION 35.5 wt % Sm



2 81 CD22590

Figure 1.



OPTICAL MICROGRAPH OF 25  $\mu\text{m}$  PARTICLE  
SIZE HIP'ed MAGNET AFTER TREATMENT AT  
1108 °C FOR 3 HOURS. NOMINAL COMPO-  
SITION 35.5 wt % Sm.



Figure 2.

Various thermal treatments were given to a number of samples from each of the 25  $\mu$ m HIPed ingots using a separate sample for each of the treatments. The magnetic properties of variously treated samples are summarized in Table 2, from which the following observations are made:

- (1) HIP at 950°C temperature induced a healing effect on the grains (similar to the sintering procedures at over 1100°C) with  $H_{ci}$  values in the range of 20 kOe.
- (2) Thermal treatments of 950°C for 62 hours, 1050°C for 24 hours, and 1108°C for 3 hours, each followed by 900°C aging and quick cooling produced higher values of coercivities.
- (3) Furnace cooling of the samples treated at 950°C degraded the coercivities significantly for lower Sm composition magnets (35.5 and 36.0 percent). The degradation was much less severe for the higher compositions (36.5 and 37.0 percent). The latter two samples are therefore expected to have a lower flux decay rate.
- (4) The  $B_r$  values show a decrease as the Sm-content is increased, as was expected because of the lowering of cobalt content. The slight changes in  $B_r$  values after different thermal treatments for a given composition, however, are believed to be due to slight inconsistencies in the alignment in the long cylindrical rods from which the various samples were cut, and not due to the thermal treatment itself.
- (5) The uniqueness of these magnets as opposed to those made by sintering<sup>(9)</sup> are the nearly constant  $H_{ci}$  values over the entire range of composition of 35.5 to 37.0 weight percent Sm except, in one case, where the samples were furnace-cooled after a thermal treatment.

- (6) Microscopic examination of the HIPed magnets showed increasing amounts of  $\text{Sm}_2\text{Co}_7$  phase with increasing Sm-content. The 35.5 percent Sm, 25  $\mu\text{m}$  particle microstructure is shown in Figure 2. This is very similar to Figure 1, except for the smaller grain size. But in both the figures, the phase composition is consistent with the chemical composition.
- (7) The composition of all the HIPed samples was in the 2-phase field of  $\text{Sm}_2\text{Co}_7$  and  $\text{SmCo}_5$ . The presence of  $\text{Sm}_2\text{Co}_7$  promotes densification during sintering at lower temperatures than would be necessary otherwise. The densification during HIP, on the other hand, is accomplished by means of compressive force, and therefore the role of  $\text{Sm}_2\text{Co}_7$  in determining densification is expected to be minimal in this case.

### 3.3 Flux Stability Measurements

Measurement of flux decay rate had begun at the end of the last reporting period. Additional experimental measurements have been performed since then, and some significant improvements in the flux stability have been observed as a result of a few selected heat treatments of the magnets which were designed to lower the amount of dissolved oxygen in the  $\text{SmCo}_5$  lattice. However, work is hampered by a lack of: (1) enough experimental facilities for flux decay rate measurement, and (2) facilities with the versatility needed for our purpose.

In order to obtain meaningful data, the experiment to measure the average decay rate of a given set of samples is usually carried on for as long as three months. With only one experimental apparatus available for such measurements, no more than about four measurements can be performed during a twelve month period. This is insufficient capability to determine the scientific basis for the flux decay mechanism in a short period of time. The large number of samples required for a single measurement in the present apparatus as also the way they are mounted in the magnetic circuit makes it difficult to give additional thermal

treatments, and it is nearly impossible to remagnetize the samples in situ. Both of the above operations would be possible in a new design conceived at CSDL some time ago.

Since measurements were limited to a very small number, it was necessary to be highly selective in choosing discrete samples with very specific thermal treatments in order to obtain significant information to determine the mechanism underlying the flux decay rates. The results obtained so far tend to indicate that the decay of flux in these magnets is a possible manifestation of the precipitation reaction of the dissolved oxygen in the  $\text{SmCo}_5$  lattice. However, much more work needs to be done to ensure absolute confidence regarding this interpretation.

Flux decay rate measurements during this period have been made on a high coercivity die-pressed sintered magnet (no. 24) after several different thermal treatments prior to magnetization, and on one HIPed (no. H-5) magnet after a thermal optimization treatment followed by furnace cooling before magnetization. The thermally optimized intrinsic magnetic properties of the two magnets are shown in Table 3.

Table 3. Magnetic properties of no. 24 and no. H-5.

|                     | no. 24 | no. H-5 |
|---------------------|--------|---------|
| $B_R$ (KG)          | 7.6    | 8.1     |
| $H_{ci}$ (kOe)      | 44.0   | 27.0    |
| $H_k$ (kOe)         | 33.5   | 12.0    |
| $(BH)_{max}$ (MGoe) | 14.4   | 16.0    |
| wt % $O_2$          | 0.6    | 0.3     |

2/81 CD22602

Prior to machining of the material for producing flux decay rate measurement samples, the thermal treatments shown in Table 4 were given to the no. 24 sintered magnets and H-5 HIP magnets. These treatments produced the magnetic properties shown in Table 3.

Table 4. Thermal treatments of sinter no. 24 and HIP H-5.

| Magnet        | Thermal treatment                      |
|---------------|--|
| Sinter no. 24 | 1110°C-3 hr, 900°C-24 hr, quick cooled |
| H-5           | 1000°C-75 hr, 900°C-4 hr, quick cooled |

2/81 CD22606

Two sets of flux stability samples of sinter number 24 and one set of H-5 were machined following the thermal treatments shown in Table 4. Of the two sets of number 24 samples, set number 2 (24-2) was given a stress-relieving thermal treatment of 480°C for 3 hours and this was followed by slow cooling. The set 24-1 was given a high temperature treatment of 1090°C for 2 hours followed by aging at 900°C for 24 hours and then was quick cooled. Quick cooling of samples was performed by pulling the samples out to a water cooled zone in the muffle, whereas slow cooling involved leaving the samples in the hot zone of the muffle after the furnace was turned off.

The samples were then magnetized in a 140 kOe field and were mounted on the outside wall of a Carpenter C-49 alloy cylinder. The mounting involved a bonding with an epoxy and curing at 150°C for 16 hours. The magnet cylinder was then introduced into a torque generator circuit and rotated at a constant speed over a period of time. The temperature of the measurement apparatus was carefully controlled at 140°F  $\pm 0.1^\circ\text{F}$ . The output voltage, which is proportional to the magnetic flux, was recorded. The decline of this voltage was then a direct measure of the decay of the magnetic flux. The change in the value of



this voltage expressed as parts per million of the initial value was plotted in a linear scale against log of time expressed in decades of days. With the proper empirical selection of zero time, the data could be represented by a straight line. The slope of the line gave the decay rate in ppm/decade of days.

After taking the initial data on sample 24-1 well into the second decade of time, the magnet assembly was taken out of the torque generator and given a 225°C treatment for 16 hours, and further decay rate data were taken on the set for approximately 110 days. The decay rate was observed to decrease about 10 percent of the previous value. Next, the magnet samples were removed from the C-49 mount and given the following heat treatment: 1108°C for 3 hours, lowered temperature to 900°C and held there for 24 hours. If the samples were quick cooled at this point, the magnets would be restored to the original structural condition with magnetic properties identical to those found during the first decay rate measurement experiment. Instead of quick cooling from the 900°C aging treatment, this time the samples were slow cooled. The slow cooling results in further precipitation of dissolved oxygen as  $\text{Sm}_2\text{O}_3$ , and in formation of  $\text{Sm}_2\text{Co}_{17}$ , which causes some degradation of the coercivities, both  $H_{ci}$  and  $H_k$ .<sup>(2)</sup> If, however, the decay of flux with time is dependent on phenomena such as oxygen precipitation and relief of residual stress, then such a treatment should produce a lower decay rate. The measurements of decay rate on 24-1 samples following the above thermal cycling did indeed significantly improve the flux stability.

After machining, the HIPed samples (H-5) were given a stress relief and structure restoration treatment at 1050°C followed by a 900°C aging and slow cooling. It is suspected that the slow cooling decreased the  $H_{ci}$  and  $H_k$  values shown in Table 1. The flux decay rate measurements of both the HIP H-5 and various thermally treated sinter magnets number 24 are presented in Table 5.

Table 5. Flux decay rate of H-5 and sinter no. 24 magnets.

| Sample Number | Heat Treatment After Machining Before Magnetization               | Heat Treatment After Magnetization and Mounting | Days From Last Heat Treatment To Start Of Measurement | Zero-time - Days Added To Start Of Measurement for Straight Line | Measurement Period - Days | Decay Rate $\frac{\rho_p}{\rho_o}$ / decade of days |
|---------------|---|---|---|--|---------------------------|---|
| 24-2          | 480°C-3 hrs furnace cooled  | Bonding + 150°C-16 hrs                          | 15  | 15   | 35                        | 813 ppm   |
| 24-1-1        | 1090°C-2 hrs, 900°C-24 hrs, quick cooled                          | Bonding + 150°C-16 hrs                          | 29  | 6  | 27                        | 761   |
| 24-1-2        | Above mounted sample, 225°C-16 hrs following previous measurement |   | 60  | 20   | 110                       | 693   |
| 24-1-3        | 1108°C-3 hrs, 900°C-24 hrs, furnace cooled                        | Bonding + 150°C-16 hrs                          | 25  | 25   | 35                        | 280   |
| H-5           | 1050°C-2 hrs, 90°C-24 hrs, furnace cooled                         | Bonding + 150°C-16 hrs                          | 9   | 9  | 49                        | 162   |

2/81 CD22603

### 3.4 Discussion and Conclusions Regarding Flux Stability Measurements

The linear relationship between the flux decay and time plotted on a log scale was suspected. When the data was plotted using the zero time as the time of start of the experiment, the resultant curve showed smaller slope at the beginning with increasing slope as time went on. It also appeared that if the experiment was run for a very long time (for example, about 4 decades of days), a log plot would eventually become a straight line with a constant slope. In order to obtain the desired result with measurements of shorter duration, one had to add some numbers of days to the starting time of measurement. That is what was done to obtain the straight line which showed the smallest deviation of the individual data points from a straight line. In Table 5, it is seen that three out of five sets of data could be reduced to the linear relationship if the starting time was assumed to be the time of the last heat treatment. Two sets of data, e.g., 24-1-1 and 24-1-2, show that the zero time started sometime after the last heat treatment.

It should also be noted that from the time the samples had seen their last heat treatment they were stored at room temperature ( $\sim 23^{\circ}\text{C}$ ), which was considerably less than the measurement temperature of  $60^{\circ}\text{C}$ . Since the chemical reaction at  $23^{\circ}\text{C}$  is bound to be much slower, and therefore negligible, than at  $60^{\circ}\text{C}$ , the linear relationship should have been obtainable almost from the beginning of the measurement cycle at  $60^{\circ}\text{C}$ . The aging at  $150^{\circ}\text{C}$  for 16 hours to cure epoxy used for bonding may be responsible for making it appear that the start was actually earlier than the start of the measurement. To obtain more meaningful data, the sample should be stored at the temperature of measurement and should not be allowed to experience an appreciably higher temperature (as during the curing of the epoxy bonding) even for a short duration, which gives an aberration to the recorded data. It is, of course, not possible to do so with the present apparatus.

The difference in the decay rate between 24-1-1 and 24-1-2 indicates that thermal stabilization would have to be carried out at a substantially higher temperature than 225°C to achieve lower decay rate. The high decay rate seen in sample 24-2 is most probably due to higher residual stresses because of incomplete removal of machining effects by the 480°C thermal treatment.

The lowest values of decay rates were seen in H-5 and 24-1-3. Both of these sets were furnace cooled from the aging temperature of 900°C. Although this treatment decreases both  $H_{Ci}$  and  $H_k$ , it does so by precipitating a portion of dissolved oxygen from the  $SmCo_5$  lattice. The lower the dissolved oxygen, the lower would be the subsequent precipitation. Therefore, it appears that the lower the oxygen content in solid solution in  $SmCo_5$ , the lower would be its decay rate. Any thermal treatment which reduces dissolved oxygen (and residual stresses) is expected to provide more stable performance. The fact that the higher stabilities were achieved in these magnets as a result of thermal treatments, which in effect lowered the  $H_{Ci}$  and  $H_k$  values, contradicts the conclusion by Mildrum and Wong<sup>(10)</sup> that higher  $H_k$  values produce higher stability.

The total oxygen contents in sinter number 24 and HIP H-5 were 0.6 weight percent and 0.3 weight percent respectively. The belief at this time is that the oxygen content would have to be substantially reduced below these values in order to achieve a goal of even higher stability. In a program funded by NASA, we are now trying to develop a powder preparation and encapsulation technique which is expected to yield HIP'ed  $SmCo_5$  magnets with extremely low oxygen content. Combining the efforts of both the ONR and NASA programs should allow us to reach the goals of very high stability for the ONR magnet program.

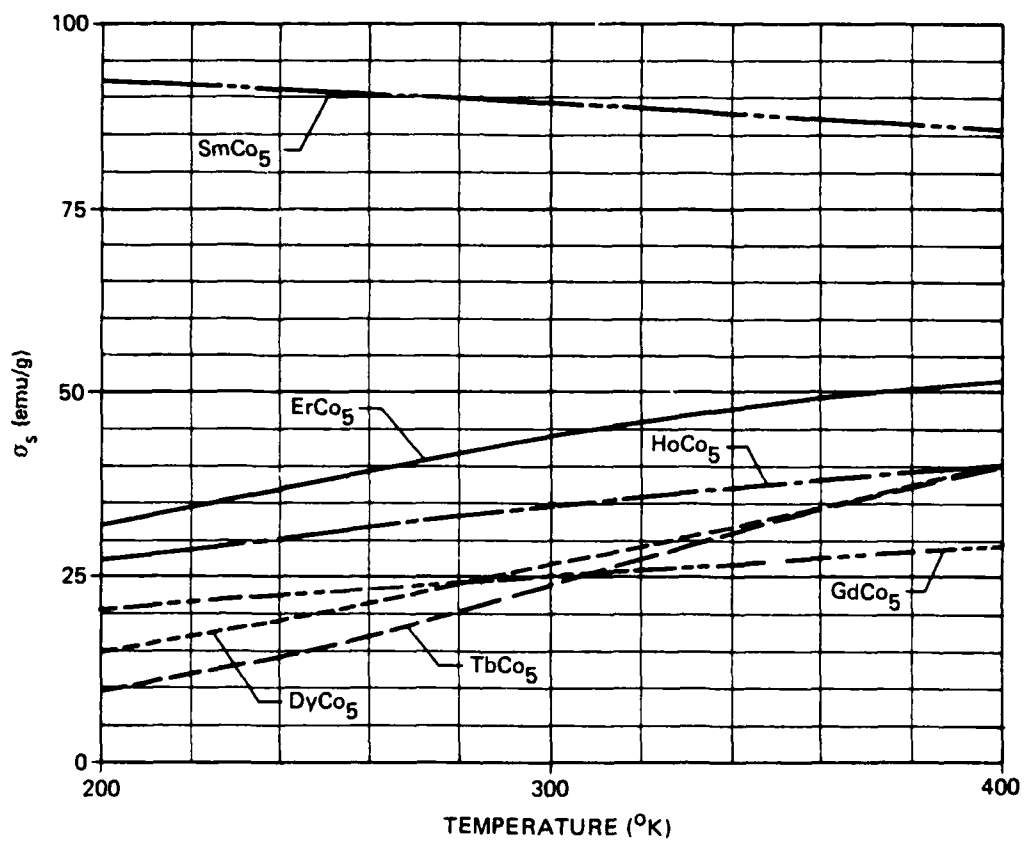
### 3.5 Temperature Compensated $SmCo_5$ Magnets

Loss of residual induction of a magnet, when taking it up to an elevated temperature below its Curie temperature, is composed of two

parts: irreversible and reversible. On cooling down to room temperature, the reversible loss is restored, but the irreversible loss can be regained only by remagnetization, provided there has been no structural change caused by the thermal cycling. Assuming that to be the case, the magnet, after the first thermal treatment, will retrace the same induction versus temperature curve on repeated thermal cycling between room temperature and the particular higher temperature.

$\text{SmCo}_5$  shows a continuous decrease of flux at a rate of approximately 400 ppm/°C within a temperature range of room temperature (RT) to 250°C. All heavy rare earth - cobalt alloys (HRE)  $\text{Co}_5$ , such as  $\text{ErCo}_5$ ,  $\text{HoCo}_5$ ,  $\text{DyCo}_5$ ,  $\text{GdCo}_5$ , and  $\text{TbCo}_5$ , have an initial increase before they start to decrease towards zero at temperatures below the Curie temperature.(11,12) From the above two references the data was replotted on saturation magnetization of the (HRE)  $\text{Co}_5$  compounds along with those of  $\text{SmCo}_5$  for the temperature range of 200°K to 400°K in Figure 3, which included the temperature of interest. Because of the opposite signs of temperature coefficients between that of  $\text{SmCo}_5$  and the HRE  $\text{Co}_5$ , one would expect that a rare-earth composition balanced between Sm and any of the HREs would result in a zero temperature coefficient.

Studies done elsewhere(3,13) have shown such results using the two HRE elements Gd and Ho in conjunction with Sm. It takes approximately 20 percent Ho or 40 percent Gd to achieve a near-zero temperature coefficient. The slopes of  $\text{TbCo}_5$  and  $\text{ErCo}_5$  appear to be much higher than either  $\text{HoCo}_5$  or  $\text{GdCo}_5$ . It is therefore expected that a much smaller amount of  $\text{ErCo}_5$  or  $\text{TbCo}_5$  would achieve the zero temperature coefficient. The result, of course, will be that not as much of the energy product need be sacrificed. This is important in view of the fact that almost 50 percent of the energy product is lost when perfect temperature compensation is brought about by the addition of  $\text{GdCo}_5$ . In the case of  $\text{HoCo}_5$  the loss is still a third of the energy product. With  $\text{ErCo}_5$  and  $\text{TbCo}_5$  the loss of energy product is expected to be less than what has been found with  $\text{HoCo}_5$  and  $\text{GdCo}_5$ .



12/77 CD13030

Figure 3. Magnetization as a function of temperature for SmCo<sub>5</sub> and several (HRE)Co<sub>5</sub> compounds.

### 3.5.1 Experimental

The experiments carried out during the reporting period consisted of experimental determination of compositions in the two ternary systems Er-Sm-Co and Tb-Sm-Co for zero temperature coefficient, and devising a method for rapid measurement for screening the composition.

#### 3.5.1.1 Measurement Apparatus

The principle used for the apparatus was the measurement of the change of flux in a gap, the flux being provided by the magnet being investigated. A double gap iron yoke was built, with a variable gap to accommodate the magnet and a fixed dimension gap where a high sensitivity Hall probe was located to measure the flux. A cutaway schematic drawing of the apparatus is shown in Figure 4. The gap with the magnet was located in a kerosene bath whose temperature could be varied over the range of 130°F to 170°F and controlled to within  $\pm 0.1^\circ\text{F}$ . The Hall probe gap was located in the upper chamber whose temperature was also controlled to a preselected constant value within  $\pm 0.1^\circ\text{F}$ , by means of water, ice, and a controlled speed stirrer. Thermocouples were located strategically to obtain precise measurement of the magnet and the Hall probe temperature. The instrumentation consisted of: (1) controlled variable speed motor for the stirrer, (2) temperature controlled kerosene bath, and (3) high precision digital read-outs of thermocouples and Hall probe output. The complete assembly is shown in Figure 5.

#### 3.5.1.2 Determination of Temperature Compensated Magnet Composition

For gyro applications the temperature compensation is required for the small temperature range of 140°F to 160°F. From the magnetization versus temperature curves shown in Figure 3, rough estimates of the

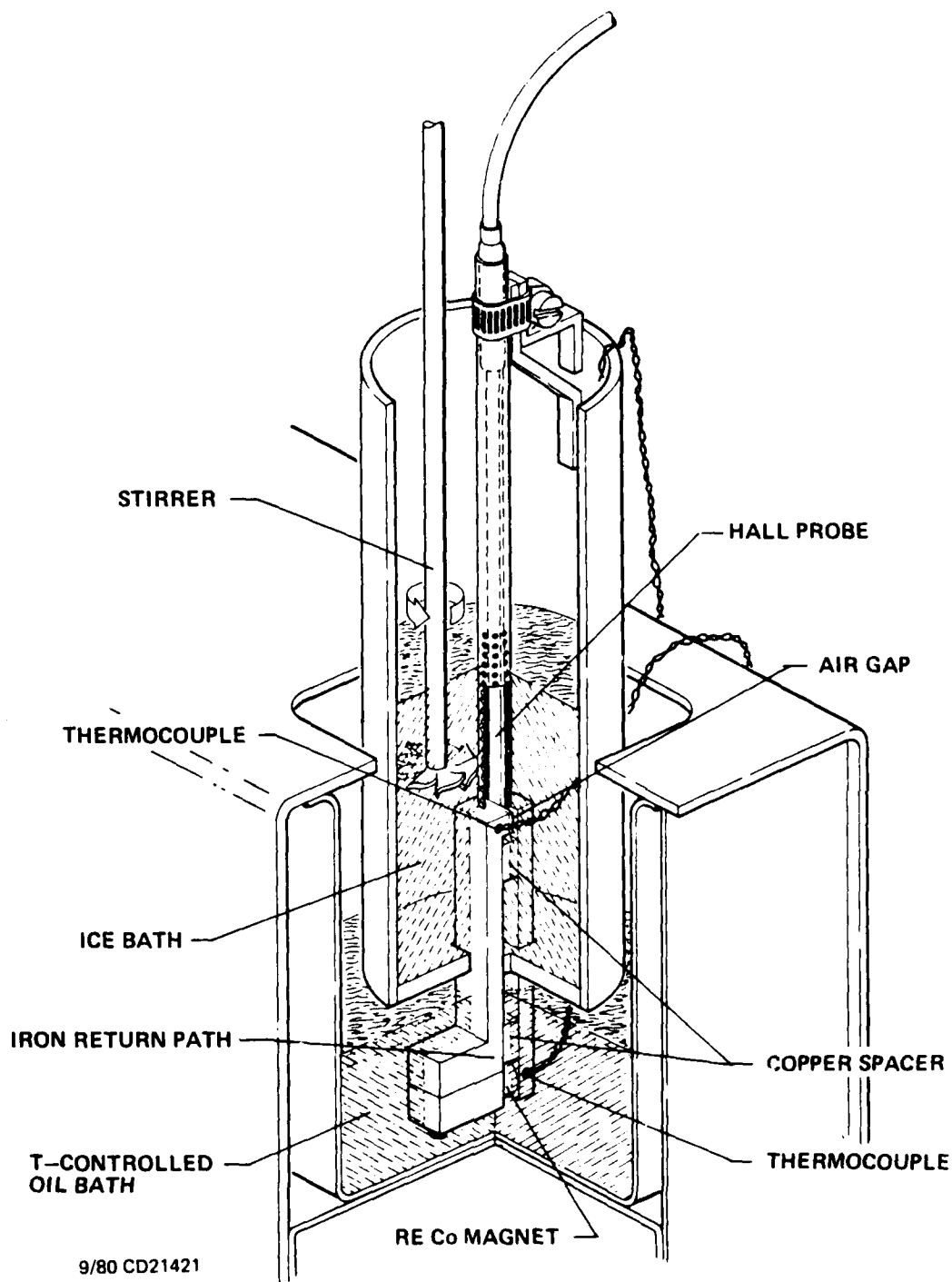
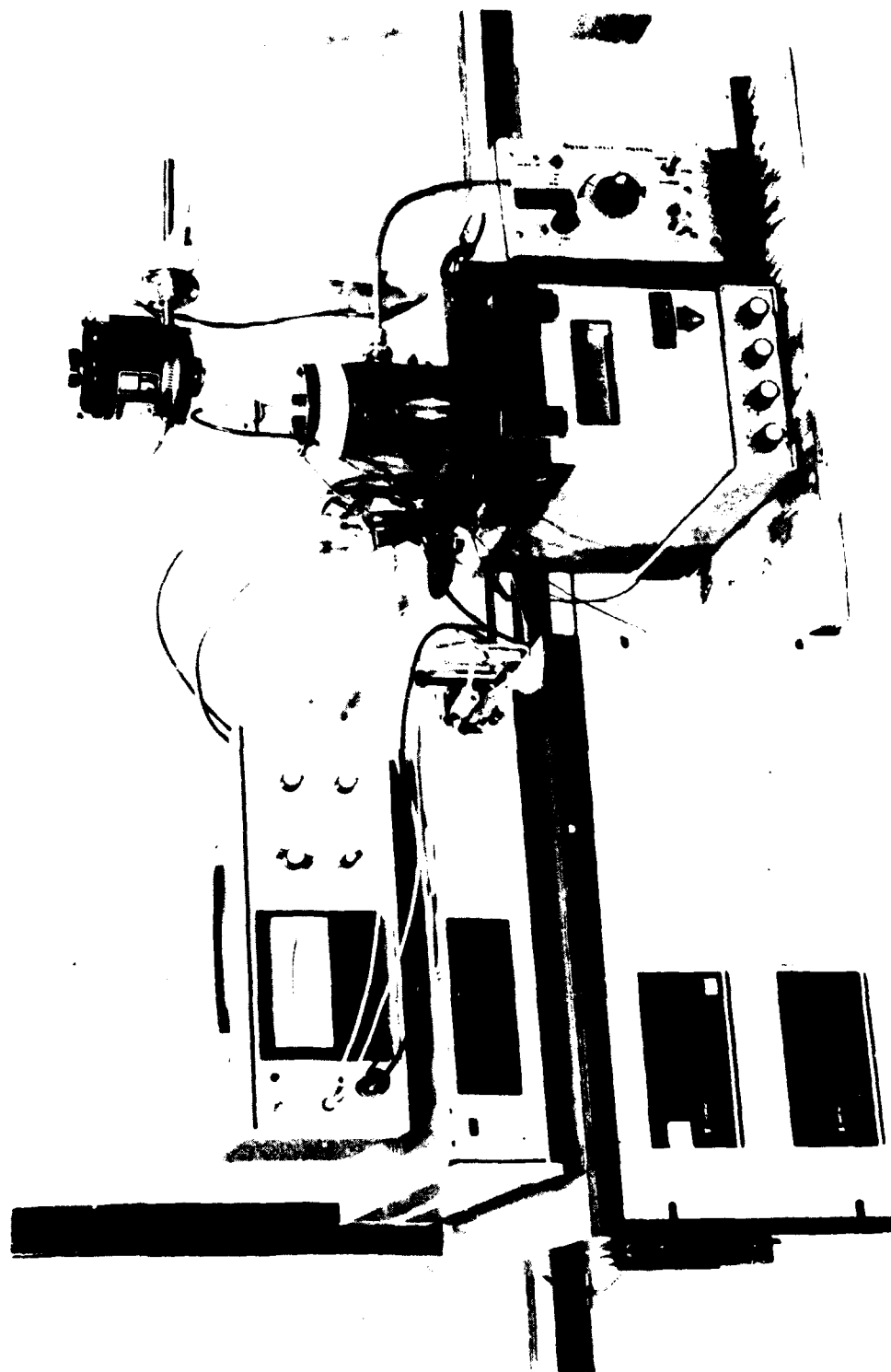


Figure 4. A cutaway schematic view of the apparatus for magnetic temperature coefficient.





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Figure 5. An overall view of the Temperature Coefficient Measurement Facility, showing temperature controllers and measurement instruments.

composition (expressed in weight percent of the respective compound) for zero coefficient were determined to be:

(1) 33.3%  $\text{ErCo}_5$  + 66.7%  $\text{SmCo}_5$

(2) 18.2%  $\text{TbCo}_5$  + 81.2%  $\text{SmCo}_5$

For the initial experiments, powder mixtures of  $\text{ErCo}_5$  +  $\text{SmCo}_5$  and  $\text{TbCo}_5$  +  $\text{SmCo}_5$  were prepared to give compositions on both sides of the compositions indicated above. Since the magnets were to be prepared by the sintering technique, the compositions were further adjusted with a 42.0 percent Sm alloy to maintain a 36.5 percent Sm equivalent of the rare earth elements, while still maintaining the  $\text{ErCo}_5/\text{SmCo}_5$  and  $\text{TbCo}_5/\text{SmCo}_5$  ratios as shown in Table 6.

Table 6. Compositions of sinter mixtures.

| Mixture No. | $\text{ErCo}_5$ wt % | Mixture No. | $\text{TbCo}_5$ wt % |
|-------------|----------------------|-------------|----------------------|
| Er-1        | 23.3                 | Tb-1        | 8.2                  |
| Er-2        | 28.3                 | Tb-2        | 13.2                 |
| Er-3        | 33.3                 | Tb-3        | 18.2                 |
| Er-4        | 38.3                 | Tb-4        | 23.2                 |
| Er-5        | 43.3                 | Tb-5        | 28.2                 |

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Table 7. Measured and theoretical  $B_r$  of Er-Sm-Co and Tb-Sm-Co magnets.

| wt % Er of Total RE | Theor. $B_r$ (G) | Measured $B_r$ (G) | wt % Tb of Total RE | Theor. $B_r$ (G) | Measured $B_r$ (G) |
|---------------------|------------------|--------------------|---------------------|------------------|--------------------|
| 23.3                | 8800             | 6950               | 8.2                 | 9400             | 7500               |
| 28.3                | 8550             | 6400               | 13.2                | 9050             | 7100               |
| 33.3                | 8300             | 5600               | 18.2                | 8650             | 6750               |
| 38.3                | 8150             | 5450               | 23.2                | 8300             | 5300               |
| 40.0                | 8000             | --                 | 28.2                | 7950             | 5350               |
| 43.4                | 7800             | 5000               | 40.0                | 7100             | --                 |

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Several discs of each of the above compositions were prepared by die pressing in a 20 kOe aligning field. They were sintered at various temperatures. As indicated by the shrinkage of the die pressed discs, fairly good sintering for the Tb containing mixtures was obtained at sintering temperatures of 1130°C and higher. Er containing samples did not sinter well at even 1140°C, but were physically strong enough for both hysteresis loop as well as temperature coefficient measurements.

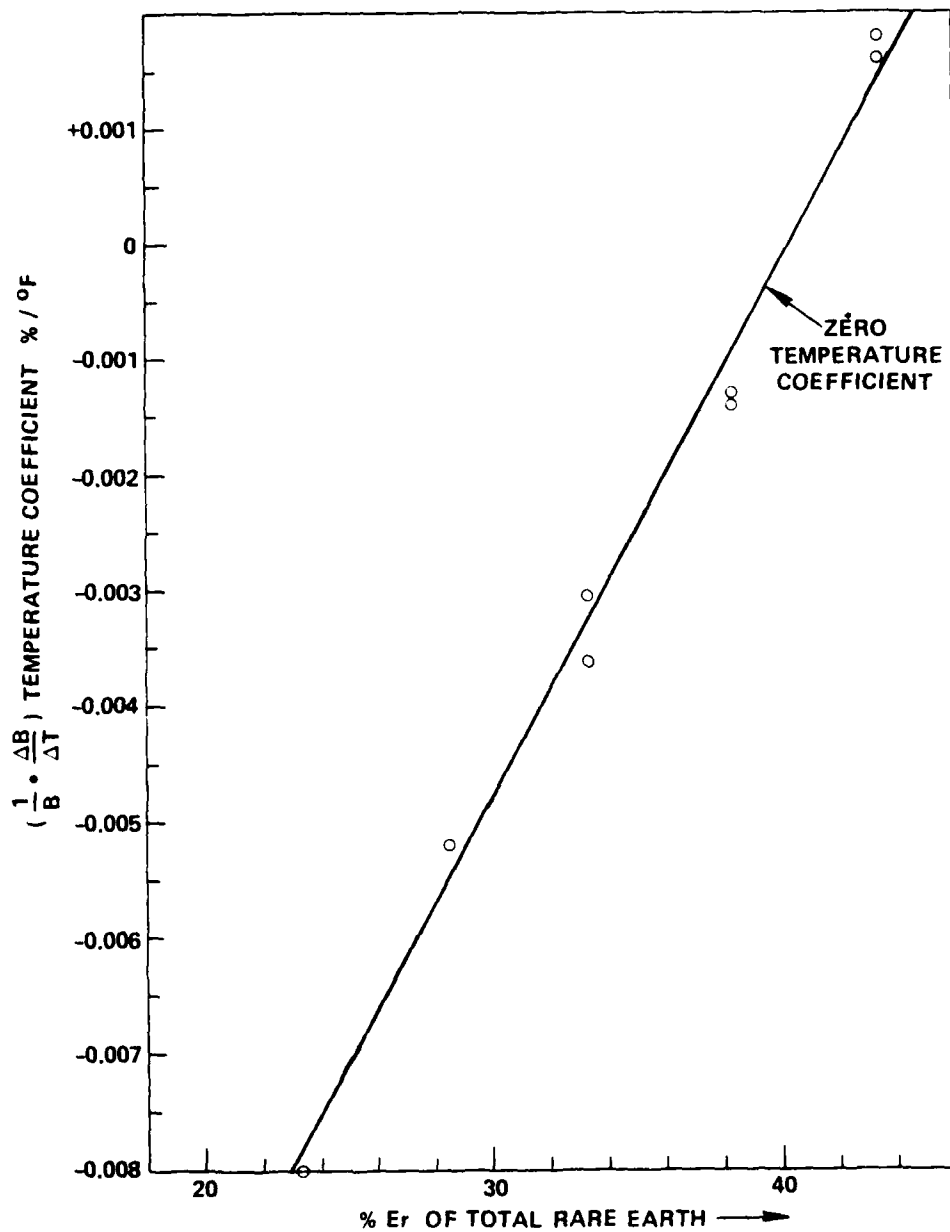
### 3.5.2 Results and Discussion

The two parameters of significance in these magnets are  $B_r$  and the temperature coefficient. The values of measured  $B_r$  are shown in Table 7 along with the theoretical values. In Figures 6 and 7 the temperature coefficients of Er and Tb respectively have been plotted against composition.

There are some discrepancies that were observed between measured and calculated values. The calculated values were based on reported properties in literature.

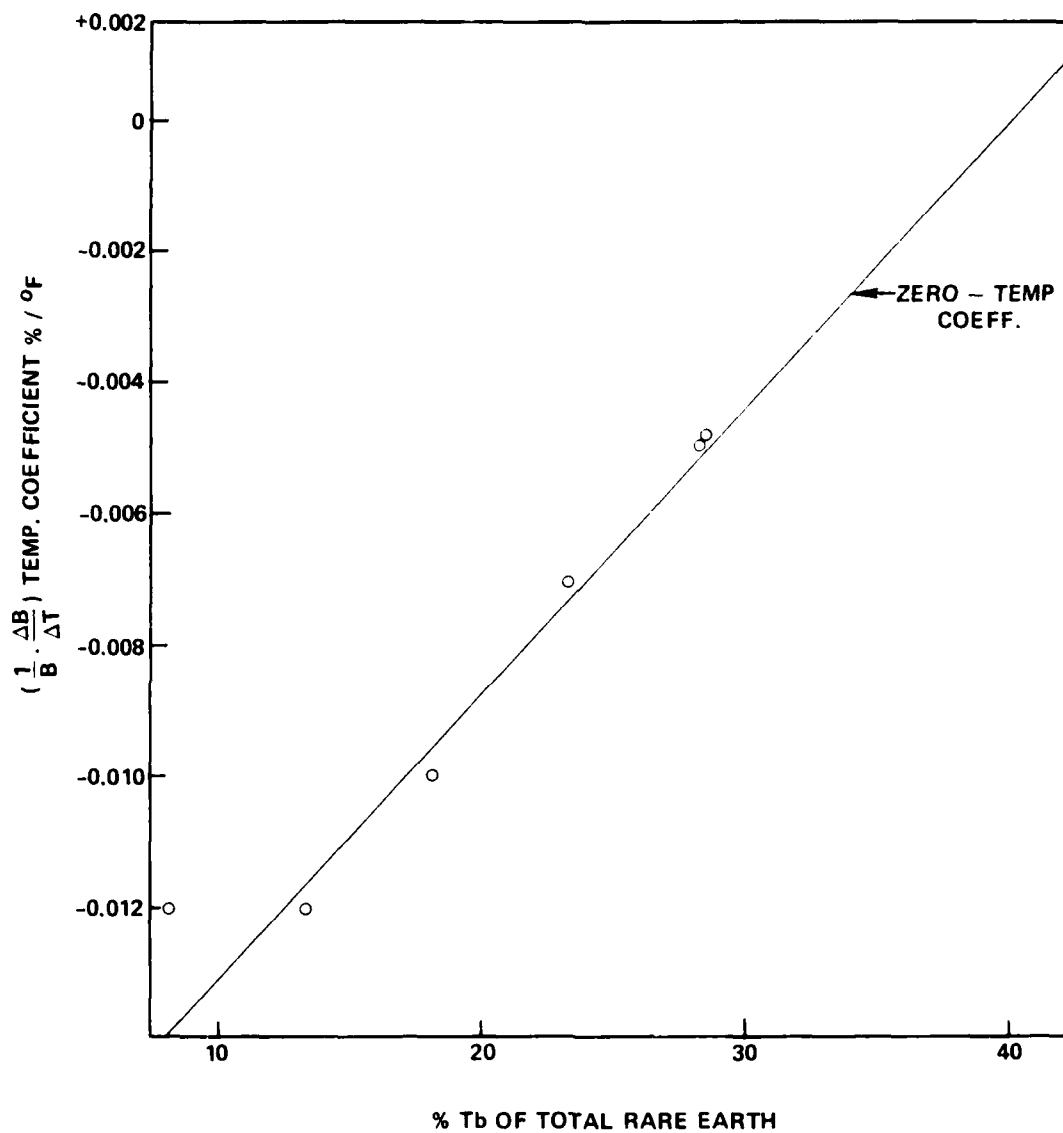
1. Zero temperature coefficients should have occurred at 33.3 percent Er and 18.2 percent Tb. From our results, the zero coefficient appears to be at 40 percent for either ternary system.
2. The measured values of  $B_r$  are substantially below the calculated values.

The die-pressed sintering technique used did not appear to produce satisfactory densification. Low  $B_r$  values could be explained on this basis and also due to poor alignment. HIP processing will undoubtedly remove some of the problem associated with the low  $B_r$  values. We do not, however, expect to solve the problem relating to composition by HIP processing. To explain this problem it will be necessary to determine the intrinsic properties of both  $\text{ErCo}_5$  and  $\text{TbCo}_5$  including their relationships between magnetization and temperature. We expect to concentrate on these areas in the ensuing period.



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Figure 6. Composition vs. magnetic temperature coefficient of Er-Sm-Co magnets. Zero temperature coefficient is shown by interpolation of data.



2/81 CD22579

Figure 7. Composition vs. magnetic temperature coefficient of Tb-Sm-Co magnets. Zero temperature coefficient is shown by extrapolation of data.

### 3.6 Thermal Expansion Control of SmCo<sub>5</sub> Magnets

One of the stated objectives of this program was to tailor the thermal expansion coefficient of the magnet to match that of beryllium. The purpose for this matching would be to reduce stresses at the bonded interface between the magnet and the beryllium support structure. For the magnet, the plane perpendicular to the magnetization direction is expected to be bonded to a beryllium surface, which would be the basal plane of the SmCo<sub>5</sub> hexagonal crystal. The thermal expansion coefficient of beryllium is  $6.6 \times 10^{-6}/^{\circ}\text{F}$ . The coefficient values for SmCo<sub>5</sub>(4) magnets are as follows:

|                         |                                       |
|-------------------------|---------------------------------------|
| Parallel to C-axis      | $3.1 \times 10^{-6}/^{\circ}\text{F}$ |
| Perpendicular to C-axis | $7.1 \times 10^{-6}/^{\circ}\text{F}$ |
| Isotropic               | $4.7 \times 10^{-6}/^{\circ}\text{F}$ |

Since both the sintered and HIPed magnets are produced from aligned and cold compacted SmCo<sub>5</sub> powder, the plane perpendicular to the magnetization direction should have a thermal expansion coefficient  $\mu$  much greater than  $4.7 \times 10^{-6}$  and somewhat less than  $7.1 \times 10^{-6}$ .

It was decided to determine the thermal expansion coefficients of some of the SmCo<sub>5</sub> magnets that had been produced in the laboratory, as well as that of HIP 50 type beryllium. The results are shown in Table 8.

The thermal expansion values shown in Table 8 indicate that the best match with beryllium is obtained from the HIPed magnet and sinter sample number 20. It is felt that we have an adequate match of thermal expansion to avoid mechanical stress problems. It is also reassuring that energy product of the magnet will not have to be sacrificed in achieving the goal of thermal expansion match.

Table 8. Thermal expansion coefficients of some  
CSDL  $\text{SmCo}_5$  magnets

| Sample Number | Type*         | $B_r$ (KG) | $(BH)_{\max}$ MGOe | Thermal Expansion Coefficient in Basal Plane |
|---------------|---------------|------------|--------------------|--|
| H-26          | HIP           | 9.2        | 21.0               | $6.7 \times 10^{-6}/^\circ\text{F}$          |
| 24            | D.P. Sintered | 7.6        | 14.5               | $6.3 \times 10^{-6}/^\circ\text{F}$          |
| 16            | D.P. Sintered | 7.8        | 15.0               | $6.2 \times 10^{-6}/^\circ\text{F}$          |
| 20            | D.P. Sintered | 8.4        | 17.5               | $6.5 \times 10^{-6}/^\circ\text{F}$          |
| --            | HIP Be        | ---        | ---                | $6.6 \times 10^{-6}/^\circ\text{F}$          |

2/81 CD22608

- \*HIP - hot isostatically pressed.  
D.P. Sintered - die pressed and sintered.  
CIP sintered - cold isostatically pressed and sintered.

However, we are now in the process of generating temperature compensated magnets by replacing a portion of  $\text{SmCo}_5$  with either  $\text{ErCo}_5$  or  $\text{TbCo}_5$ . Once high energy product magnets are obtained from these two ternary systems, the thermal expansion matching problem will require examination once again.

### 3.7 Future Plans

- (1) Continue studies on flux decay mechanisms.
- (2) Further improvement of flux stability
  - (a) Lowered oxygen content using facilities being built at CSDL under a NASA contract
  - (b) Further refinement of thermal treatments

- (3) Continue studies with HIPed temperature compensated magnets
  - (a) Determine necessary alloy composition
  - (b) Determine magnetic properties
  - (c) Establish optimum thermal treatment
  - (d) Measure decay rate and thermal expansion coefficient
- (4) Process standardization
- (5) Try ONR  $\text{SmCo}_5$  magnets in CSDL instruments



## SECTION 4

### Sm<sub>2</sub>Co<sub>17</sub> MAGNET INVESTIGATIONS

#### 4.1 General

This task was included in the program in November 1979. Its objective is to investigate the feasibility of employing arc-plasma-spraying as a process for producing Sm<sub>2</sub>Co<sub>17</sub> type magnets of binary Sm-Co compositions with coercivities considerably higher than the 1 to 2 kOe that are obtained through the conventional sintering process. Examination of plasma spraying for Sm<sub>2</sub>Co<sub>17</sub> magnet fabrication was mainly motivated by our earlier successes with the SmCo<sub>5</sub> composition.

#### 4.2 Background

Low values of the intrinsic coercivity,  $H_{ci}$ , and  $H_k$  (= value of the reverse field that corresponds to 90 percent of the remanent magnetization in the second quadrant) are known to be generally related to poor long-term and short-term magnet flux stability.<sup>(10,14)</sup> Large  $H_{ci}$  values reflect a strong resistance to demagnetizing forces and large  $H_k$  values indicate square loop demagnetization behavior.

Sintering is the most widely used technology for producing SmCo<sub>5</sub> and Sm<sub>2</sub>Co<sub>17</sub> type magnets. The sequence of operation includes generation of fine alloy powder, alignment and compaction of this powder in an applied magnetic field, and sintering of the compact to achieve high density. This technique is presently capable of producing SmCo<sub>5</sub> magnets with  $(BH)_{max}$  of 16 to 20 mGOe<sup>(15)</sup> and Sm<sub>2</sub>(TM)<sub>17</sub> magnets with energy products of about 30 mGOe.<sup>(16)</sup> (TM = Transition Metal.) In each of these instances, however, the value of  $H_{ci}$  measured is considerably lower than what appears to be theoretically possible with these materials. The maximum  $H_{ci}$  attainable is indicated by the value of the measured anisotropy field,  $H_A$ , in these materials. These values are about 350 kOe for SmCo<sub>5</sub> and close to 100 kOe for Sm<sub>2</sub>Co<sub>17</sub>.<sup>(17)</sup> The

actual values obtained in these materials for sintered magnets are in the range of 15 to 35 kOe for  $\text{SmCo}_5$ , 1 to 2 kOe for  $\text{Sm}_2\text{Co}_{17}$ , and only about 5 to 6 kOe for modified  $\text{Sm}_2\text{Co}_{17}$  compositions. These low  $H_{ci}$  values have been attributed by various researchers to effects arising from oxidation, microcracking and grain growth.<sup>(7)</sup> While these low  $H_{ci}$  values may be suited for some general applications, they are particularly discouraging for applications that demand constant flux over extended periods of time.

The origins of oxidation, microcracking, and grain growth can be traced to the processing that is employed in the fabrication of this material. For effective alignment, compaction, and sintering, the starting powder material needs to be of extremely fine size (less than 10 microns). Because of the large overall surface area introduced by reduction of the powder to these fine sizes, a substantial amount of oxygen pick-up is observed. Even after taking extreme precautions, oxygen levels in excess of 0.35 to 0.5 weight percent are found in the powder and therefore in the resulting magnets.<sup>(18)</sup> Typical commercial magnets, however, have up to 2 weight percent oxygen. To avoid the harmful effects of oxygen (because of a resulting depletion of the rare earth) excess Sm is added to the overall composition. While this adjusts the gross composition, it also results in the formation of cobalt-depleted regions through an oxygen dissolution and reprecipitation process.<sup>(6)</sup> These are low coercivity regions that permit easy magnetization reversal in the material resulting in a lower measured  $H_{ci}$  value.<sup>(6,19)</sup>

Effects related to microcracking are more subtle and less understood. Since microcracking results in the formation of extra surface (and, therefore, more defects), it appears that microcracks will be sources of reverse domain nucleation and growth. These microcracks are believed to result from the same processes that result in crack formation during processing of brittle ceramics.<sup>(8)</sup> Both macro- and micro-stresses (related to high quenching rates and thermal expansion anisotropy respectively) are believed to lead to stress concentrations that result in crack formation. Slow cooling is, therefore, the

preferred mode of treatment following high temperature exposure.(19,20) Micro-stresses relating to anisotropic thermal expansion of  $\text{SmCo}_5$  are believed to be responsible for striation formation in this material at intermediate temperatures.(20) Microcrack formation is an indication of the level of stresses (macro- and micro-) present in the material. These stresses may be an additional source of low coercivity.

The strong dependence of  $H_{ci}$  on grain size is believed to be related to the increased amount of defects present in the average grain of the large grain sized material.(5) Since the smaller the grain size the smaller the probability for occurrence of a defect, small grain size material is expected to (and appears to indeed have) higher coercivity. Some grain growth is unavoidable in commercial magnets (which are produced by sintering) during shrinkage and densification of the compact. Even when great care is taken during sintering, the final grain size is about 20 to 30 microns as opposed to a pre-sintered average particle size of less than 10 microns. Experiments have also shown that the sintered material is very inhomogeneous chemically because of which large scale second phase precipitation occurs at intermediate temperatures resulting in considerably reduced values of  $H_{ci}$ .(20)

All of the effects discussed above are known to play a strong role in determining  $H_{ci}$  in  $\text{SmCo}_5$  magnets. While the analysis is equally valid for magnets produced with  $\text{Sm}_2\text{Co}_{17}$  type compositions, these aspects take on added significance in the fabrication of this latter material. Experimental efforts to produce reasonably high  $H_{ci}$   $\text{Sm}_2\text{Co}_{17}$  magnets have so far been very disappointing.

#### 4.3 Rationale for Adopted Approach

The single most important parameter for successful inertial applications is magnet flux stability at gyro operating temperatures. Initial experiments at CSDL have shown that sprayed  $\text{SmCo}_5$  magnets show a remarkably lower rate of flux decay than do commercial magnets.(21)

This is primarily the result of the very high quality of material that has been produced in this program. Sprayed  $\text{SmCo}_5$  magnets, however, are isotropic and, therefore, the energy product of these magnets is close to half of what is obtained in the aligned, commercially fabricated material. To obtain a higher amount of flux from these magnets, one needs to either introduce texture in the deposits or to shift the material composition towards higher cobalt content (by spraying  $\text{Sm}_2\text{Co}_{17}$  type of deposits).

An isotropic  $\text{Sm}_2\text{Co}_{17}$  magnet is expected to show an energy product of about 10 to 12 MGOe as opposed to 7 to 9 MGOe measured in isotropic  $\text{SmCo}_5$  material and 16 to 18 MGOe found for aligned commercial  $\text{SmCo}_5$  magnets. An aligned  $\text{Sm}_2\text{Co}_{17}$  magnet would obviously show much higher values.

To date, efforts employing sintering of aligned magnets have been unsuccessful in fabricating magnets with acceptable levels to the intrinsic coercivity ( $H_{ci}$ ). The maximum value of  $H_{ci}$  measured on binary  $\text{Sm}_2\text{Co}_{17}$  sintered material is about 1 to 2 kOe as opposed to a theoretical maximum possibility of about 100 kOe.<sup>(17)</sup> In contrast, CSDL's sprayed  $\text{SmCo}_5$  magnets have exhibited coercivities of 68 kOe.<sup>(7)</sup> This research deals with the production of higher values of intrinsic coercivity using the plasma spray process for isotropic  $\text{Sm}_2\text{Co}_{17}$  deposits with potential energy products on the order of 12 MGOe.

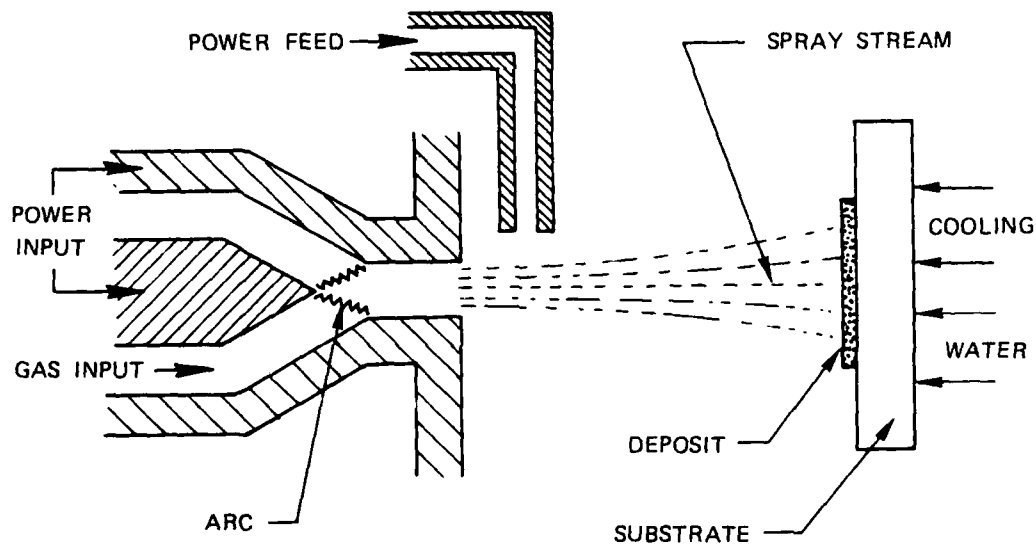
$\text{SmCo}_5$  magnets produced by spraying have demonstrated that these magnets can also be cooled slowly from high temperatures unlike sintered magnets that have to be cooled rapidly after treatment to avoid severe degradation in  $H_{ci}$  and in second quadrant demagnetization behavior.<sup>(19)</sup> This degradation has recently been shown to result from increased second phase precipitation with decreasing temperatures because of existing chemical inhomogeneities.<sup>(20)</sup> Slow cooling leads to a decreased amount of strain in the material and therefore a lower incidence of crack formation.<sup>(8,20)</sup>

The oxygen content of sprayed material is typically less than 0.2 weight percent mainly because spraying is conducted in an inert environment chamber and the starting powder (20 to 60 microns) is much larger than that used for sintering (less than 10 microns). An added advantage of this process is that while the starting size of the powder particle is large, the average grain size in the deposit is very small. Both amorphous and crystalline  $\text{SmCo}_5$  material have been produced using this technique.<sup>(22,23)</sup> Because of the fine grain size that is obtained, homogenization of the deposit occurs quite readily and very large values of  $H_{ci}$  are obtained by heating the deposited material to temperatures of 850°C to 1000°C, which are substantially lower than those required for sintering this material.<sup>(1,15)</sup> This permits the retention of very fine grain sizes in sprayed magnets on the order of about 2 to 5 microns (compared to 20 to 30 microns in sintered material).<sup>(8)</sup> All of these factors are believed to be responsible for the high  $H_{ci}$  values that have been obtained in sprayed  $\text{SmCo}_5$  material.

The foregoing suggests that it might be possible to obtain reasonably large  $H_{ci}$  values in magnets sprayed with  $\text{Sm}_2\text{Co}_{17}$  type compositions.  $H_{ci}$  values obtained in sprayed  $\text{SmCo}_5$  material are about 20 percent of the anisotropy field. If a similar achievement can be attained in sprayed  $\text{Sm}_2\text{Co}_{17}$  material, coercivities of about 15 to 20 kOe could result from such an effort (which would be larger than those obtained so far in sintered material by a factor of about 7 to 10). Such an improvement is desirable because it can result in sprayed magnets with energy products of about 10 to 12 mGOe and magnets of this type are expected to find many applications. Also, if additional subsequent efforts aimed at developing texture in these materials should prove successful, magnets with the highest magnetic properties attained so far will result.

#### 4.4 The Plasma Spray Process

A schematic sketch of this process is shown in Figure 8. The process involves striking a high intensity dc arc between two electrodes, and ionization of gases - nitrogen, hydrogen, argon, and helium - as a consequence. This forms the plasma. Upon exit through a nozzle, the plasma combines to form neutral atoms, and releases a large amount of thermal energy without an appreciable loss in gas temperature. The material to be deposited is introduced at this stage in the form of a powder. The gases impart both thermal and kinetic energy to the powder particles, thereby melting them and propelling them rapidly towards the substrate to form the deposit.



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Figure 8. Schematic sketch of spray process. (22)

#### 4.5 Results and Discussion

##### 4.5.1 Alloy Procurement

The desired compositions of the deposits (after spraying) determined the compositions selected for the starting materials. Past experience with spray fabrication of these materials has shown that roughly 3 to 5 percent samarium is lost, relative to the cobalt (depending on the starting composition), through evaporation, during spraying. Also, an additional 1 percent is sacrificed to oxygen, both as a result of some oxygen present in the starting alloy and some that is picked up during processing. (The assumption that all of the oxygen in the deposit exists as an oxide of samarium appears reasonable in that  $\text{Sm}_2\text{O}_3$  has the lowest free energy of formation amongst the several possible oxides that can be considered).

Based on these considerations, alloys with compositions containing 34.5, 25.2, and 23.5 weight percent Sm were ordered and procured from Research Chemicals, Phoenix, Arizona. It was recognized that the desired final deposit compositions should be in the range set by the stoichiometries of  $\text{SmCo}_5$  (33.8% Sm) and  $\text{Sm}_2\text{Co}_{17}$  (23.0% Sm) with the overall composition shifted towards the  $\text{Sm}_2\text{Co}_{17}$  value. The as-received alloys were examined by optical microscopy. Figure 9 shows the etched microstructures of these alloy materials. Very large grains were observed. In two of the samples the existence of a second phase was observed. In the 25.2 weight percent Sm sample, the second phase appeared to exist mainly at the grain boundaries.

##### 4.5.2 Deposit Fabrication

The alloys were crushed from ingot form to finer sizes using a laboratory jaw crusher and a double disk pulverizer. The resulting powder was sifted to select the correct size for spraying purposes. The several powders were mixed in a laboratory blender to secure as-blended

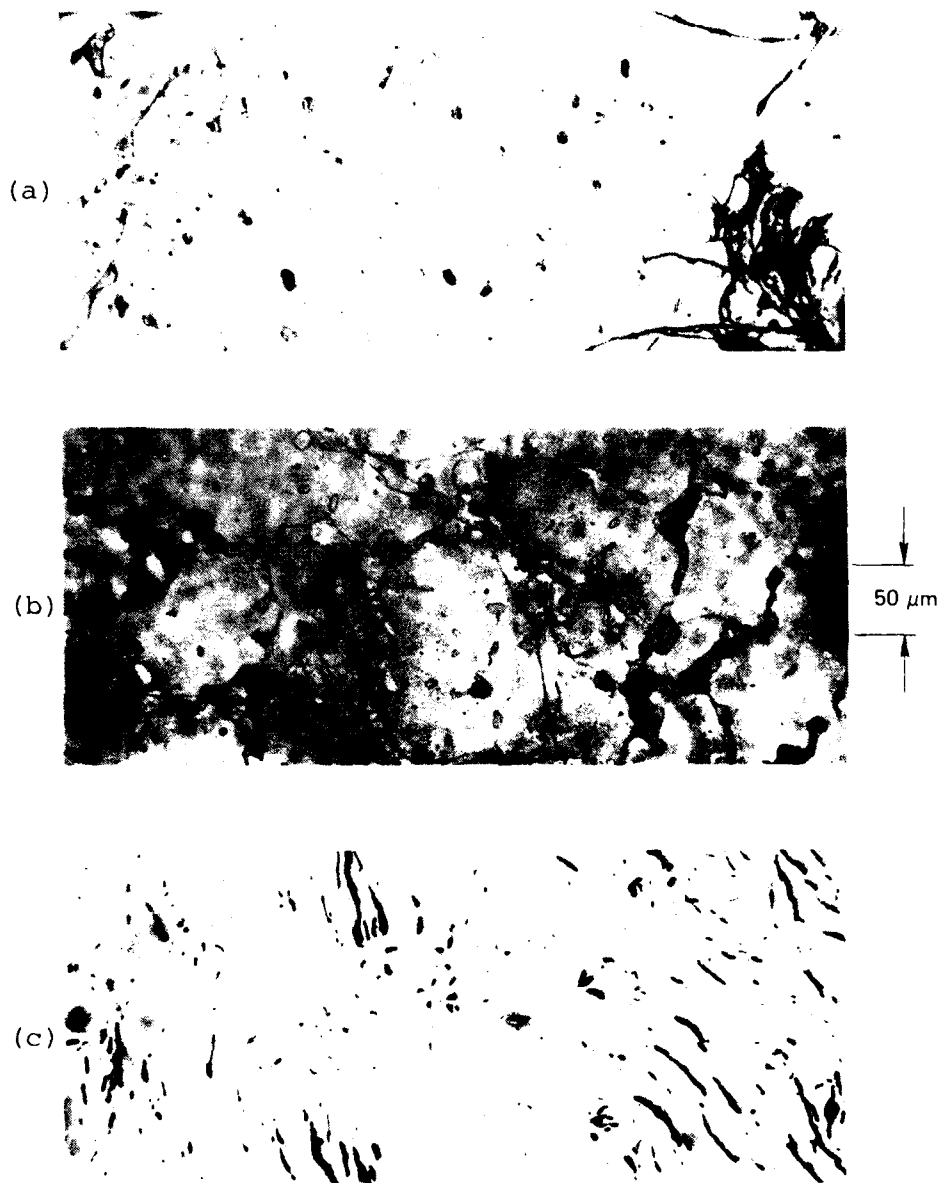


Figure 9. Etched microstructures of as-received alloy. 3. Nitral.  
 (a) 34.5; (b) 25.5; (c) 13.5. (a) and (b) show  
 existence of  $\alpha$  phase. In (b) this is distributed  
 at grain boundaries.



compositions of 34.0, 32.0, 30.0, 28.0, and 26.0 weight-percent samarium. Spray depositions were performed with these five starting powders on a copper substrate mounted on a water-cooled rotating feedthrough inside a water-jacketed, inert gas environment, plasma spray chamber. The conditions used for spraying were identical to those used previously for the  $\text{SmCo}_5$  materials. These optimized conditions have evolved gradually over the past several years with our continued involvement in the spraying of the Sm-Co materials. The thickness of the as-sprayed deposits was typically about 0.3 cm. The samples were kept reasonably thin on purpose, since a greater level of crystallinity is known to develop in plasma-sprayed deposits with increasing deposit thickness during spraying.<sup>(22)</sup> The deposited material was removed from the copper substrate and characterized using a variety of techniques.

#### 4.5.3 Microstructure

Sample pieces were removed from each of the deposits and metallographic specimens obtained to reveal the deposit cross-section. (Viewing axis was perpendicular to the plasma spray beam axis.)

Figure 10 shows the etched surfaces of the several deposit cross-sections. The nomenclature used in this report for deposit identification is 26.0 for deposits made from a starting powder of 26.0 weight-percent samarium composition, 30.0 for deposits produced from 30.0 weight-percent samarium powder, and so forth. The microstructures appear with a pancake-type morphology resulting from flattening of the molten alloy particles upon impact at the substrate.<sup>(7,22)</sup> The as-sprayed structures also contain pores (which appear as dark, almost circular, regions) and a few unmelted particles, in addition to the observed platelets which give rise to the layered microstructure. The minor differences observed for the several deposit microstructures were not considered to be very significant.

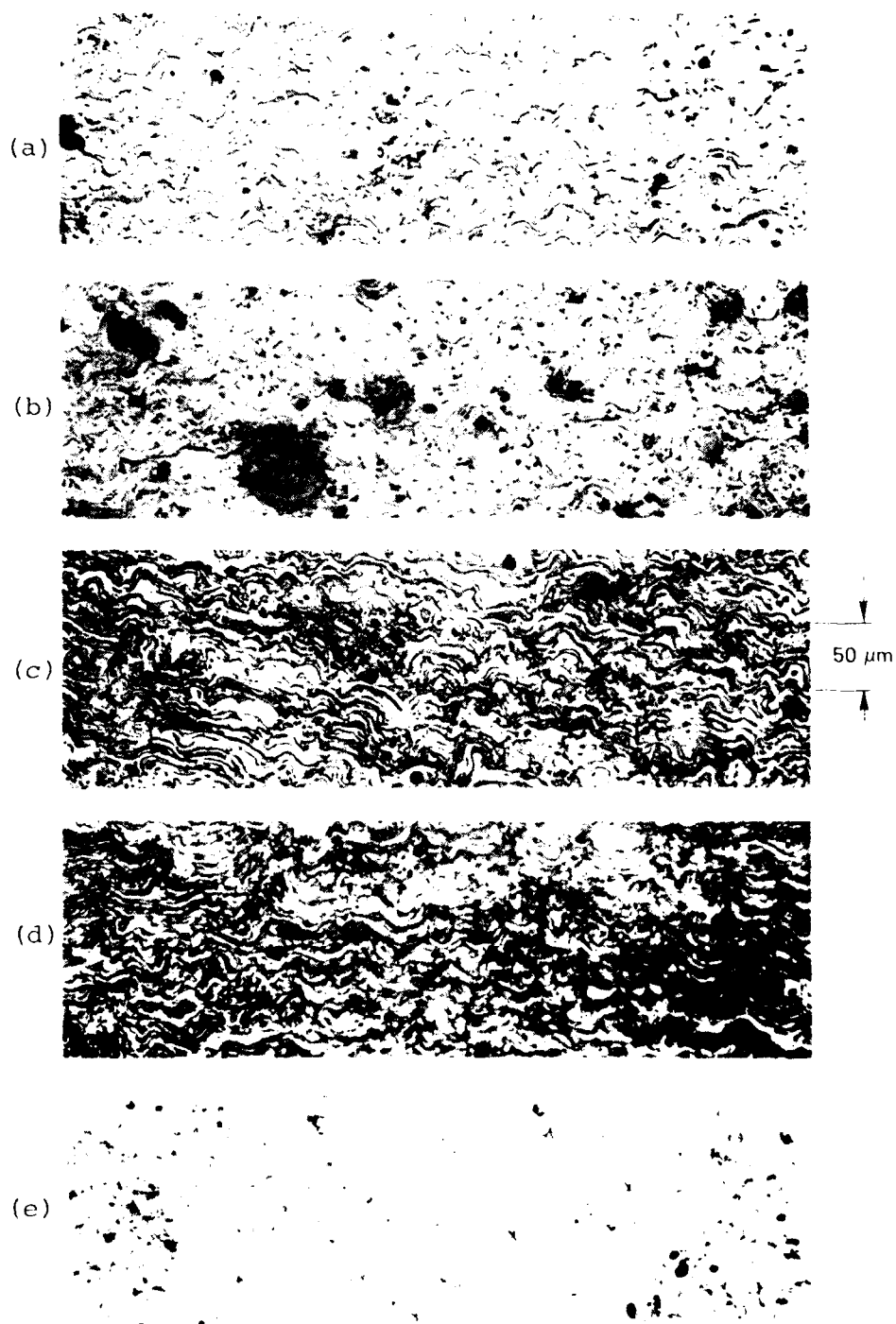
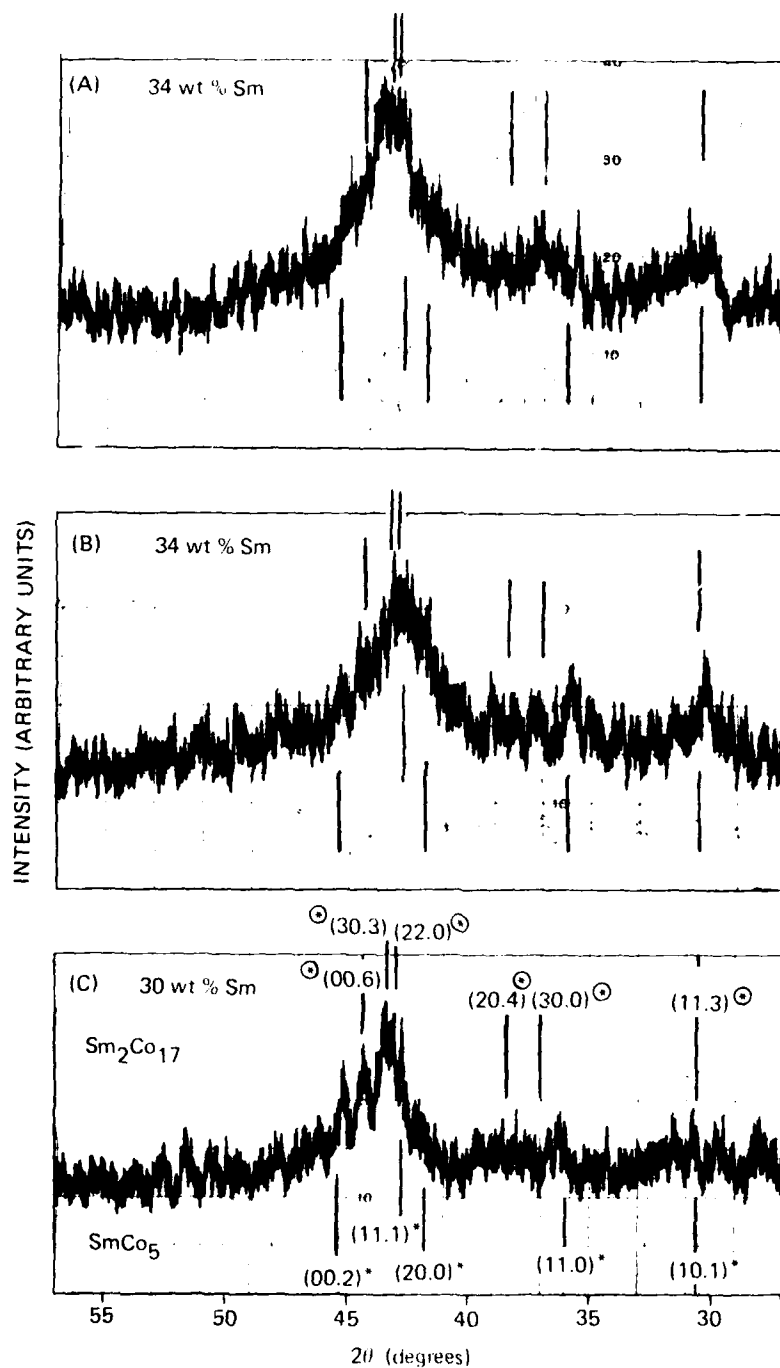


Figure 10. Microstructures of 440C steel at different temperatures. (a) 34.0°C; (b) 44.0°C; (c) 54.0°C; (d) 64.0°C; (e) 74.0°C.

#### 4.5.4 Crystal Structures

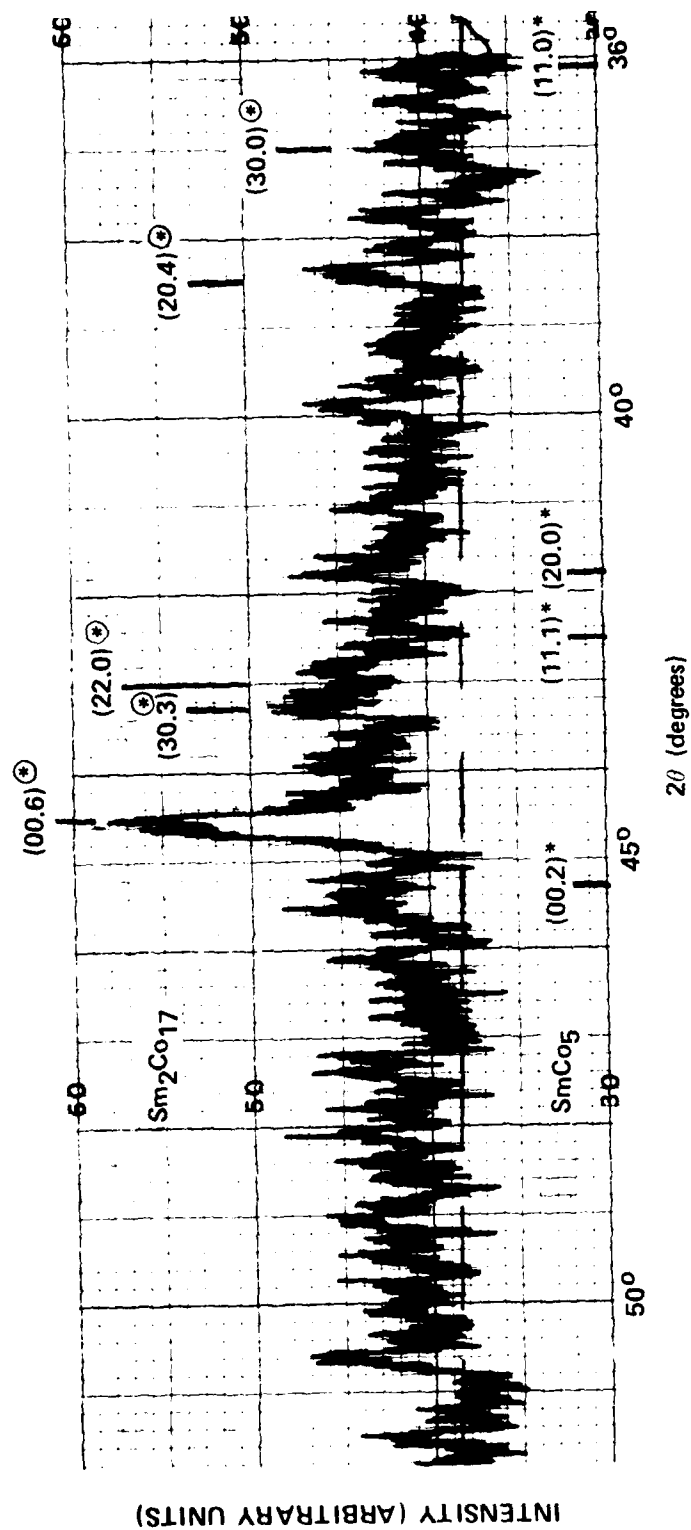
X-ray diffraction patterns were obtained on a few of the deposits fabricated with 34.0 and 30.0 weight percent Sm powder. The diffraction patterns were obtained on the flat side of the deposit closest to the substrate since that had experienced the most severe cooling during deposition. Plasma spraying is known to result in amorphous and metastable crystalline structures<sup>(22,23)</sup> and the intention was to see if an amorphous material was obtained with these compositions. The diffraction patterns obtained on three such samples are shown in Figure 11. Also included in Figure 11 are peak positions for well-crystallized  $\text{SmCo}_5$  and  $\text{Sm}_2\text{Co}_{17}$  intermetallic compounds. All of the x-ray patterns were obtained with copper radiation and a diffracted beam graphite monochromator.

Considerable broadening of the x-ray peaks was observed for all of the deposits. The diffuse patterns obtained on these materials are believed to be indicative of amorphous structures similar to what are conventionally obtained by rapid quenching techniques. The existence of a few minor crystalline peaks was interpreted to indicate the existence of a small amount of crystalline material dispersed in an otherwise amorphous material. Along these lines a most interesting, and possibly very significant, observation was made for one of the subsequently deposited 34.0 samples. The x-ray pattern obtained from the surface of this sample (shown in Figure 12) consisted of a single, sharp crystalline peak superposed on an otherwise amorphous type pattern. A single peak was interpreted as illustrative of texture in the crystalline component of the deposit. This deposit was fabricated using a starting composition of 34.0 weight percent Sm. The composition of the deposit was indicated to be about 30.0 weight percent Sm (which is in the two-phase  $\text{SmCo}_5$  -  $\text{Sm}_2\text{Co}_{17}$  region of the phase diagram), by x-ray fluorescence. The sole crystalline peak observed was found to be located at the (00.6) peak position for  $\text{Sm}_2\text{Co}_{17}$  - the compound of interest. This observation showed that it might be possible to produce crystallographically aligned  $\text{Sm}_2\text{Co}_{17}$  materials by plasma spraying, a feature that has so far eluded efforts on the  $\text{SmCo}_5$  sprayed materials.



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Figure 11. As-sprayed x-ray patterns obtained on two deposits made with 34 wt % Sm and one with 30 wt % Sm powders. Expected peak positions are identified for  $\text{SmCo}_5$  and  $\text{Sm}_2\text{Co}_{17}$  compounds using the symbols \* and @ respectively.



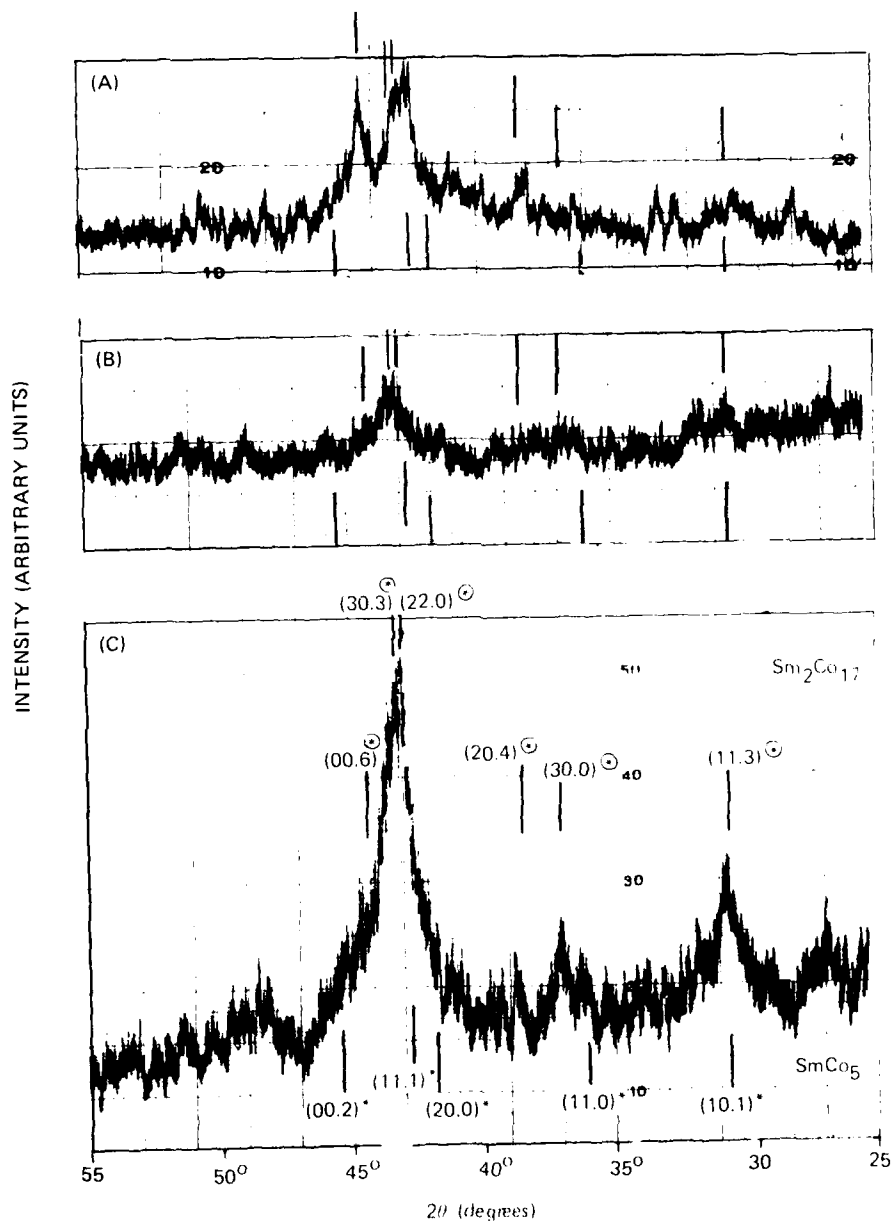
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Figure 12. X-ray pattern showing single, sharp crystalline peak superposed on an essentially amorphous pattern. Expected peak positions for  $\text{SmCo}_5$  and  $\text{Sm}_2\text{Co}_{17}$  compounds are indicated by the symbols \* and \* respectively.

Subsequent efforts at producing similar material for detailed examination have met with limited success. It appears that small changes in the cooling rate of the deposited material (induced by minor variations in experimental conditions) will affect the structure of the deposit. (Attempts are presently underway to vary the cooling conditions at the substrate.) In one instance, however, a somewhat more crystalline (possibly microcrystalline) deposit was obtained with a strong (00.6) peak. When a portion of this deposit was removed, crushed into the form of a powder and subjected to x-ray diffraction, an amorphous type pattern was observed with none of the peaks clearly identified. The (00.6) peak was found to almost disappear, indicating that the strong peak observed earlier corresponded to Bragg reflections from a relatively small volume of crystalline material that existed in the form of oriented crystallites, thereby reinforcing the total (00.6) reflection. The process of reducing the deposit into a fine powder must have resulted in producing overall random orientation of these crystallites and this showed up as a significantly reduced intensity. Both of these patterns are shown in Figure 13. This figure also contains the pattern obtained on another section of the solid as-deposited material which was subjected to a temperature of 550°C for 16 hours in argon. An increased degree of crystallinity resulted from this treatment. This was expected from past experience.<sup>(23)</sup>

#### 4.5.5 Heat Treatment and Magnetic Properties

A few discs, each 0.200 inch in diameter, were cored from each of the deposited materials using electrical discharge machining (EDM). The magnetic properties were measured for the as-sprayed condition on one set of discs. The several discs were then subjected to a series of different heat treatment conditions and the properties measured using maximum applied static magnetic fields up to 140 kOe. Both temperature as well as time at temperature were varied and the effects resulting from such treatments are discussed below.



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Figure 13. X-ray patterns of film-deposited sample: (A) As-sprayed; (B) After grinding to fine powder; (C)  $550^\circ\text{C}$ , 10 hrs. annealed.

#### 4.5.5.1 Effect of Temperature

A series of exposures at successively higher temperatures were employed for the several deposited samples. Time at each temperature was fixed at 16 hours. After each thermal exposure the power to the furnace was shut off and the heat-treated discs allowed to cool slowly inside the furnace. The magnetic properties measured after the different heat treatments are listed in Table 9. This table also shows the properties measured on these materials after a high temperature exposure of 1100°C followed by an aging treatment at 850°C. (Temperatures far in excess of 1100°C are used when sintering is employed as the fabrication process). The observed variation of  $H_{C1}$  with temperature of exposure is further plotted in Figure 14.

#### 4.5.5.2 Effect of Time at Temperature

Another set of as-sprayed discs was next exposed to varying time at a fixed temperature of 600°C. Again, as before, the power to the furnace was shut off after each exposure and the heat-treated samples allowed to cool slowly inside the furnace. The magnetic properties measured after these latter treatments are shown in in Table 10. The variation of  $H_{C1}$  with time of exposure is shown in Figure 15.

Several interesting observations were made from the tabulated and plotted magnetic data. These are briefly discussed below.

- (1) Substantial improvements were observed for the magnetic properties with the low temperature treatments. These were attributed to increased homogenization and grain growth through crystallization-related processes.

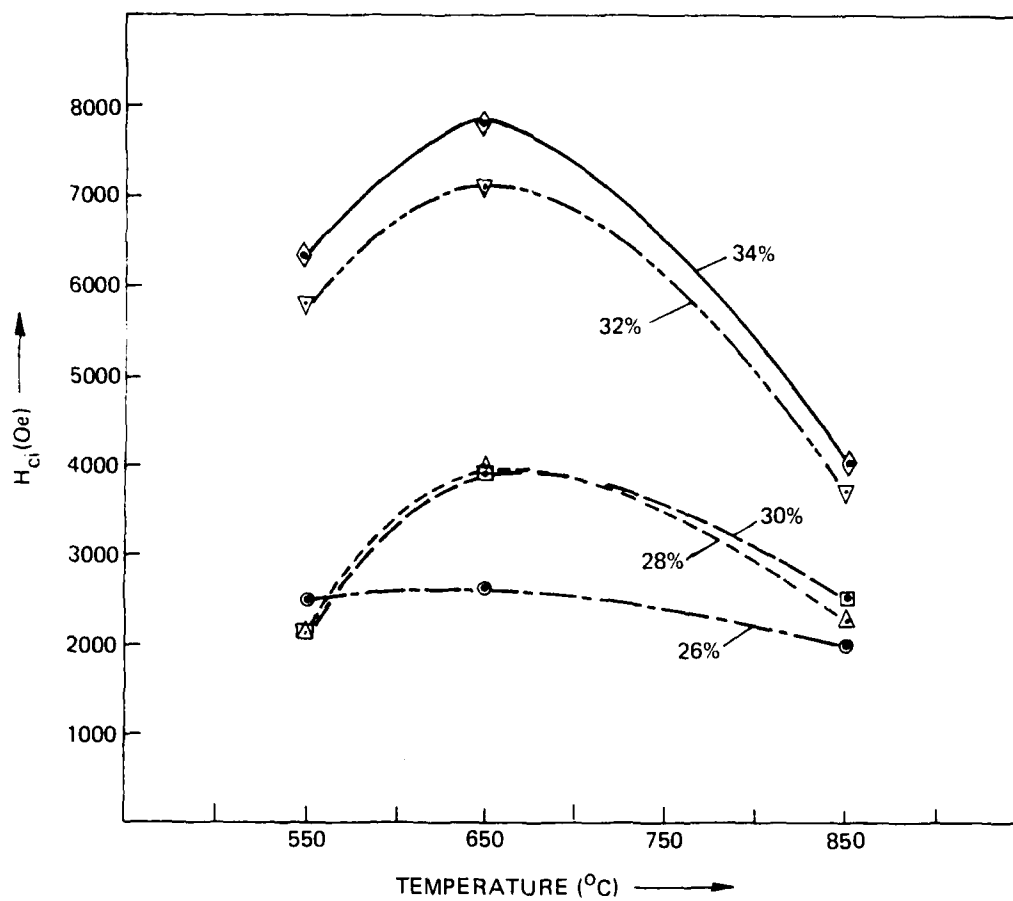


Table 9. Effect of temperature of treatment.

| Sample | Heat Treatment   | $B_r$ (G) | $4\pi M_D$ (G)* | $H_c$ (Oe) | $H_{ci}$ (Oe) | (BH) <sub>max</sub> (MGOe) |
|--------|--|-----------|-----------------|------------|---------------|----------------------------|
| 34.0   | (A): As-sprayed  | 5800      | 9100            | 1700       | 2400          | 2.5                        |
| 32.0   |  | 5600      | 8750            | 2300       | 4250          | 3.2                        |
| 30.0   |  | 4700      | 8350            | 2300       | 3800          | 2.7                        |
| 28.0   |  | 6650      | 10000           | 1500       | 2100          | 2.5                        |
| 26.0   |  | 4300      | 10300           | 1000       | 1300          | 1.0                        |
| 34.0   | (A) +<br>(B): 550°C, 16 hrs                                  | 5750      | 8600            | 3150       | 6300          | 4.5                        |
| 32.0   |  | 5750      | 8500            | 2850       | 5850          | 4.1                        |
| 30.0   |  | 5600      | 9800            | 1400       | 2050          | 3.5                        |
| 28.0   |  | 5950      | 9550            | 1500       | 2100          | 2.2                        |
| 26.0   |  | 5100      | 8500            | 1850       | 2500          | 2.4                        |
| 34.0   | (A) + (B) +<br>(C): 650°C, 16 hrs                            | 5900      | 7400            | 4100       | 7800          | 6.0                        |
| 32.0   |  | 6000      | 7450            | 3900       | 7150          | 6.0                        |
| 30.0   |  | 5950      | 8700            | 2600       | 3900          | 4.0                        |
| 28.0   |  | 6100      | 8700            | 2700       | 4000          | 4.0                        |
| 26.0   |  | 5250      | 8450            | 2000       | 2600          | 3.0                        |
| 34.0   | (A) + (B) + (C)<br>(D): 850°C, 16 hrs                        | 5300      | 6900            | 2750       | 4000          | 3.5                        |
| 32.0   |  | 5300      | 6950            | 2650       | 3700          | 3.5                        |
| 30.0   |  | 5550      | 7900            | 1800       | 2500          | 2.5                        |
| 28.0   |  | 5550      | 7950            | 1900       | 2300          | 2.5                        |
| 2600   |  | 5050      | 8200            | 1600       | 2000          | 2.0                        |
| 34.0   | (A) + (B) + (C) +<br>(D): 1100°C,<br>2 hrs; 850°C,<br>24 hrs | 3500      | 6600            | 1200       | 1800          | 1.0                        |
| 32.0   |  | 3700      | 6600            | 1200       | 1900          | 1.1                        |
| 30.0   |  | 3450      | 7650            | 600        | 700           | 0.5                        |
| 28.0   |  | 3200      | 7460            | 600        | 600           | 0.5                        |
| 26.0   |  | 2050      | 7500            | 400        | 500           | 0.2                        |

\*  $4\pi M$  value at 15 kOe field strength on demagnetization portion of  $4\pi M$  versus  $H$  curve.

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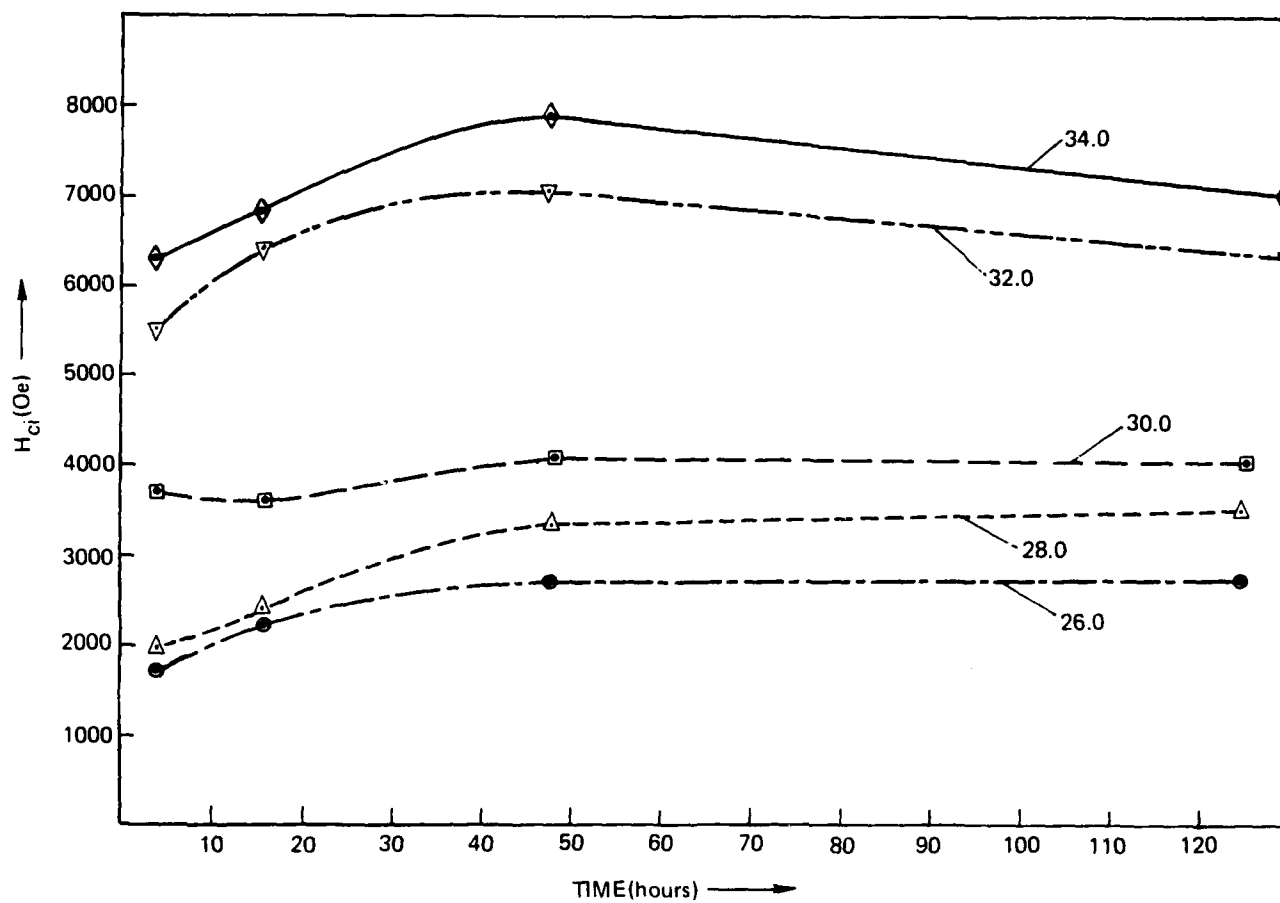
Figure 14. Effect of temperature of treatment on  $H_{ci}$  (for fixed time = 16 hours).

Table 10. Effect of time at temperature.

| Sample | Heat Treatment                                    | $B_r$ (G) | $4\pi M_D$ (G) * | $H_C$ (Oe) | $H_{Ci}$ (Oe) | $(BH)_{max}$ (MGoe) |
|--------|---|-----------|------------------|------------|---------------|---------------------|
| 34.0   | (A) : As-sprayed +<br>(B) : 600°C, 4 hrs          | 6400      | 8650             | 2900       | 6300          | 4.7                 |
| 32.0   |   | 6300      | 8600             | 2700       | 5500          | 4.3                 |
| 30.0   |   | 5600      | 8300             | 2400       | 3700          | 3.4                 |
| 28.0   |   | 6350      | 9700             | 1500       | 2000          | 2.4                 |
| 26.0   | (A) + (B) +<br>(C) : 600°C, 12 hrs                | 5550      | 10230            | 1200       | 1700          | 1.7                 |
| 34.0   |   | 5900      | 7950             | 3100       | 6800          | 4.0                 |
| 32.0   |   | 6300      | 8350             | 3100       | 6400          | 4.9                 |
| 30.0   |   | 5300      | 8100             | 2300       | 3600          | 3.0                 |
| 28.0   | (A) + (B) + (C) +<br>(D) : 600°C, 32 hrs          | 5600      | 9050             | 1700       | 2400          | 2.4                 |
| 26.0   |   | 5500      | 9700             | 1600       | 2200          | 2.2                 |
| 34.0   |   | 6500      | 8200             | 4050       | 7900          | 6.6                 |
| 32.0   |   | 6500      | 8350             | 3700       | 7050          | 6.0                 |
| 30.0   | (A) + (B) + (C) +<br>(D) + (E) : 600°C,<br>77 hrs | 5900      | 8500             | 2700       | 4100          | 4.0                 |
| 28.0   |   | 6550      | 9400             | 2300       | 3400          | 3.8                 |
| 26.0   |   | 5900      | 9750             | 1900       | 2700          | 2.8                 |
| 34.0   |   | 6450      | 8000             | 4100       | 7000          | 6.6                 |
| 32.0   | (A) + (B) + (C) +<br>(D) + (E) : 600°C,<br>77 hrs | 6650      | 8100             | 3850       | 6300          | 6.4                 |
| 30.0   |   | 5800      | 8250             | 2650       | 4000          | 3.8                 |
| 28.0   |   | 6150      | 8900             | 2550       | 3500          | 3.9                 |
| 26.0   |   | 5700      | 9350             | 2050       | 2700          | 2.9                 |

\*  $4\pi M$  value at 15 kOe field strength on the demagnetization portion of the  $4\pi M$  versus H curve.

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Figure 15. Effect of time of exposure at 600°C on the value of  $H_{Ci}$ .

- (2) Unlike observations on similarly produced modified  $\text{Sm}_2\text{Co}_{17}$ -type compositions,<sup>(24)</sup> the dependence of the thermal treatment required (for producing optimum coercivity) on deposit composition was found to be at best minimal. These observations indicated that grain size played a strong role in determining  $H_{ci}$  of these binary compositions.
- (3) The largest value of  $H_{ci}$  measured for these binary Sm-Co compositions in this program was 7.9 kOe.
- (4) The high values measured for  $4\pi M_D$  in the as-sprayed condition were indicative of the amorphous nature of these deposits. As expected, these values were found to gradually decrease with increasing crystallization, which resulted from the heat treatments that were performed.

#### 4.6 Conclusions

$H_{ci}$  values of up to 8 kOe were generated in binary  $\text{Sm}_2\text{Co}_{17}$ -type compositions by using appropriately selected, low temperature heat treatments on amorphous and close-to-amorphous plasma-sprayed deposits. It was determined that amorphous material (over a reasonably broad range of composition) could be produced using this technique in agreement with earlier observations.<sup>(22)</sup> The possibility of producing  $\text{Sm}_2\text{Co}_{17}$ -type magnets with the easy magnetization axis oriented perpendicular to the plane of the deposit was indicated in this study. The existence of a sole crystalline peak, superimposed on an amorphous pattern and located at the expected peak position for the (00.6) reflection from  $\text{Sm}_2\text{Co}_{17}$ , was interpreted as indicating texture in the deposit. These suspicions were confirmed in that this peak was observed to all but disappear when a powder pattern of this material was obtained. It was concluded that the cooling conditions at the substrate significantly affected the texture in the deposit.

#### 4.7 Recommendations for Future Work

- (1) Vary cooling conditions at the substrate to study influence on deposit structure.
- (2) Examine effects of crystallizing the amorphous materials in the presence of externally applied magnetic fields and thermal gradients.
- (3) Study the influence of low temperature crystallization treatments in an hydrogen atmosphere.

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